METAL COMPLEXES OF POTENTIALLY PLANAR MULTIDENTATE LIGANDS

BY

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LIST ABBREVIATIONS

BCSAP	Bicapped Square Antiprism
DABPSC	6,6'-Diacetyl-2,2'-bipyridinebissemicarbazone
DAP	2,6-Diacetylpyridine
DAPBAH	2,6-Diacetylpyridinebisbenzoicacidhydrazone
DAPSC	2,6-Diacetylpyridinebissemicarbazone
DFBPSC	6,6'-Diformyl-2,2'-bipyridinebissemicarbazone
DHH	Decahexahedron
DHPHPY	1,4-Dihydrazinophthalazinebis(2-pyridinecarboxaldimine)
DTH	Decatetrahedron
$\|E_{hk\ell}\|$	Normalized Structure Factor Amplitude
$\|F_{calc}\|$	Calculated Structure Factor Amplitude
$\|F_{hk\ell}\|$	Observed Structure Factor Amplitude
$F_{hk\ell}$	Structure Factor
HBP	Hexagonal Bipyramidal
MCPAP	Monocapped Pentagonal Antiprism
PBP	Pentagonal Bipyramidal
PHENSC	2,9-Diformylphenanthrolinebissemicarbazone
SCA•HCl	Semicarbazide Hydrochloride
THF	Tetrahydrofuran

Abstract of Thesis Presented to the Graduate Council
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METAL COMPLEXES OF POTENTIALLY
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Reaction of the hexadentate ligand 6,6'-diformyl-2,2'-bipyridinebissemicarbazone (DFBPSC) with $La(NO_3)_3$ resulted in an eleven coordinate complex. The space group was $P\bar{1}$ with a = 8.230(4), b = 11.833(7), c = 13.805(5) Å; and α = 75.78°(4), β = 88.40°(4), γ = 89.87°(5). The final R was 5.6%. The geometry of the coordination sphere was analyzed and found to be best described as a decahexahedron. A similar reaction of DFBPSC with $Eu(NO_3)_3$ resulted in a ten coordinate complex. The space group was found to be $P2_1/n$ with a = 21.903(5), b = 15.478(6), c = 7.767(3) Å; and β = 93.75°(2). The final R was 6.1%. The difference in coordination number relative to the La(III) compound was due to the smaller ion size of Eu(III). The geometry of this ten coordinate complex was found to be best described as a bicapped square antiprism. An unusual dimeric species

resulted from reaction of DFBPSC with $Hg(NO_3)_2$. One-half of one ligand was bound to one Hg(II) ion with the other half of that same ligand bound to a second Hg(II) ion. A second ligand was similarly bound. The space group was Fddd with a = 23.291(11), b = 22.611(15), and c = 14.954(9) Å. The final R was 5.9%. The difference in coordination number relative to the Ln(III) ion complexes was discussed.

Attempts were made to synthesize and structurally characterize a di-manganese complex with 1,4-dihydrazinophthalazinebis(2-pyridine carboxaldimine) (DHPHPY). X-ray crystallographic analysis revealed no Mn(II) ion was coordinated by the ligand. The space group was $P2_1/c$ with a = 9.407(2), b = 15.082(3), c = 14.617(3) Å; and β = 96.95°(2). The final R was 6.3%. The ligand DHPHPY was found to exist in a tautomeric form different from that observed in two previous studies. The ramifications of the existence of such a tautomer relative to the coordinating ability of the ligand was discussed.

INTRODUCTION

Interest has grown in metal complexes of high coordination number and the resulting geometries produced by such complexes as indicated by a number of review articles written on the subject.[1-3] The transition metals are the most intensely studied metals, as a group, and their coordination numbers are typically four or six.[4] It is not surprising then, that a metal complex is usually thought of as exhibiting high coordination when the number of donor atoms to the metal center exceeds six.

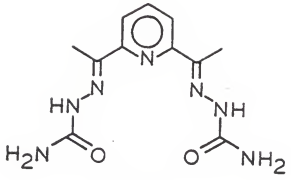
There are a number of important factors that affect the coordination number a particular metal ion can exhibit. These factors include the size of the metal ion, the steric interactions of the donor atoms or groups, the charge on the metal ion, and for many transition metals, crystal field effects. Independent of crystal field effects and for a given metal-to-donor distance, as the number of donors around a metal ion increases the distance between the donors must necessarily decrease. As the donor-to-donor distances decrease, unfavorable steric interactions become important. For metal ions of the same size but of differing charge, these steric effects are modified somewhat in the more highly charged metal ion due to an increase in the metal-to-donor bond strength. To alleviate the steric interactions

among the donors, the metal-to-donor distances can increase or a ligand can be ejected from the coordination sphere. This latter effect reduces the coordination number by one. From these simple considerations, for monodentate ligands, the highest coordination that can be achieved should be obtained with the smallest donors available coordinated to a large, highly charged metal ion. Consistent with these considerations are the experimental observations that show nine coordination for Tc[5] and Re[6] hydride complexes and nine coordination for some aquo and flouride complexes for some of the early members of the lanthanide and actinide series.[3]

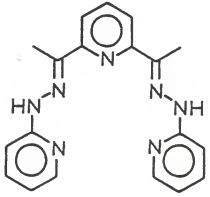
To date there are no known examples of a metal complex with a coordination number exceeding nine where only monodentate ligands are employed. More highly coordinated metal complexes have been prepared utilizing a variety of chelating agents. Indeed, such complexes have become relatively common.[1] An important aspect of the use of chelating groups in coordination chemistry is the almost unlimited flexibility they offer in the design of particular geometries. The geometrical constraints of a particular ligand are major factors in determining the geometry a metal complex will adopt. With this in mind, work was begun in this laboratory in the early 1970's to synthesize a series of compounds of the first row transition metals with pentagonal bipyramidal geometry (PBP). At this time, for many of the transition metals, not only was this particular geometry unknown but also coordination number seven was quite rare. A number of planar pentadentate

ligands were synthesized via a condensation reaction with 2,6-diacetylpyridine (DAP) and a variety of ammine and semicarbazide derivatives (Figure 1). These ligands were prepared either directly or by way of metal ion template methods to produce a series of complexes with PBP geometry.[7,8] This work produced the first reported examples of seven coordination for Fe(II), Co(II), Ni(II) and Cu(II) ions. The geometrical constraints of the ligand 2,6-diacetylpyridinebissemicarbazone (DAPSC) were such that the chloride salts of Mn(II), Fe(II), Co(II) and Zn(II) formed an isomorphous series with space group Ia. 2,6-Diacetylpyridinebissemicarbazone and the nitrate salts of Mn(II), Co(II), Ni(II) and Zn(II) formed the isomorphous series with space group $P2_1/n$. The ligand DAPSC was also used to produce PBP complexes of Hg and Cd.[9] 2,6-Diacetylpyridinebissemicarbazone and a related ligand 2,6-diacetylbisbenzoicacidhydrazone (DAPBAH) produced even higher coordination for some of the lanthanides.[10,11]

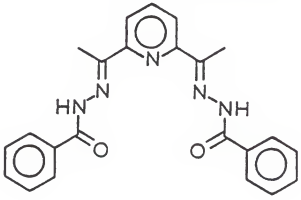
The success with the ligand DAPSC and its analogous compounds in the synthesis of PBP transition metal complexes laid the foundation for this present work. A natural extension of the structural studies with DAPSC would be to increase the number of donor atoms in the planar ligand to six by making the bipyridyl analogue (Figure 2). This ligand would then be used to attempt to synthesize metal complexes with hexagonal bipyramidal geometry (HBP).



DAPSC



2,6-Diacetylpyridinebis-2-pyridylhydrazone



DAPBAH

Figure 1

DAPSC and Other Pentadentate Schiff Base Ligands

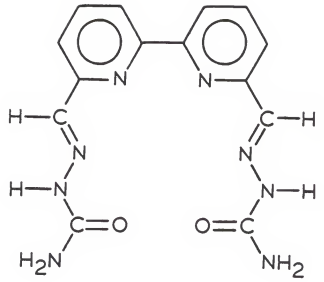


Figure 2

6,6'-Diformyl-2,2'-bipyridinebissemicarbazone

Hexagonal bipyramidal metal complexes are quite uncommon. Most of the reported examples of this geometry have been made with the uranyl ion (UO_2^{+n}) and its actinyl analogues.[12-14] The linear uranyl ion with the axial positions blocked is ideally suited for this geometry. Recently, there have been a few reports of HBP complexes of Pb(II),[15,16] Sr(II),[15] Cd(II)[16] and La(III)[17] with some Schiff base macrocycles. The geometry of the La(III) complex has been assumed on the basis of some spectral and analytical data. An x-ray study has not been made to date on this compound and its geometry is not certain.

The geometrical aspects of eight coordination has been reviewed by a number of workers.[1,18,19] That HBP complexes are uncommon is due to the fact that dodecahedral and square antiprismatic geometries are energetically more favorable on both steric and electronic[20] grounds in the absence of geometrical constraints of the ligands. It was proposed at the start of this work that the hexadentate ligand 6,6'-diformyl-2,2'-bipyridylbissemicarbazone (DFBPSC) would be ideally suited for synthesizing HBP metal complexes.

CHAPTER ONE

SYNTHESIS AND X-RAY DIFFRACTION EXPERIMENTAL

The rare earth lanthanide oxides, 99.9% pure, were purchased from the Rare Earth Division of the American Potash and Chemical Company. Reagent grade 2,6-dibromopyridine was purchased from the Fluka Chemical Company and was used without further purification. Reagent grade mercuric nitrate, purchased from the J. T. Baker Chemical Company, was a gift from Mr. Don Swieter. Reagent grade manganese chloride tetrahydrate was purchased from the J. T. Baker Chemical Company. The 2-pyridinecarboxaldehyde was purchased from the Aldrich Chemical Company 99% pure. The hydrazine hydrate, 85% solution, was purchased from Fisher Scientific as were the semicarbazide hydrochloride, anhydrous ethyl ether, and reagent grade tetrahydrofuran (THF).

The ethyl ether and THF used as solvents in the synthesis of DFBPSC were dried over sodium metal in the presence of benzophenone.[21] A navy blue to deep violet solution above the sodium indicated the solution was free of oxygen and water. These solvents were freshly distilled before use in any subsequent step.

The n-butyl lithium in pentane was purchased from the Aldrich Chemical Company. The concentration of the n-butyl lithium was determined before use by titration with a 1.09 M

s-butyl alcohol solution in xylenes with o-phenanthroline as an indicator as described by Watson and Eastham.[22]

The 1,4-dihydrazinophthalazinebis(2-pyridinecarboxaldimine) (DHPHPY) was a gift from Mrs. Ruth Palenik. It was prepared by reaction of 2-pyridinecarboxaldehyde (2.2 g, 0.020 mol) with 1,4-dihydrazinophthalazine[23] (1.9 g, 0.010 mol) in 100 mL warm chloroform. The resulting orange solid was collected and washed with ether. This solid was dissolved in 200 mL of ethanol with 2 drops concentrated HCl. Solid $MnCl_2 \cdot 4H_2O$ was added in a 2:1 mole ratio, metal to ligand. The resulting orange solid was filtered and redissolved in a 60% water, 40% ethanol solution. Slow evaporation of this solution resulted in the formation of orange crystals suitable for X-ray diffraction.

In a typical procedure 0.10 mmol of the lanthanide oxide was dissolved in excess, concentrated nitric acid. The slurry that formed initially cleared within minutes upon heating. This solution was heated to dryness, and the resulting nitrate salt was used in subsequent steps.

The following is a description of a typical reaction setup for the synthesis of 6,6'-dibromo-2,2'-bipyridine.[24] This reaction and all subsequent reactions involving the use of the n-butyl lithium were carried out in a 4 neck, 1 L round-bottom flask. The flask was equipped with a 250 mL pressure equalizing addition funnel with a rubber septum cap through which solvent was introduced via syringe. An inert atmosphere was maintained by blowing nitrogen through the system during the course of the reaction. A mechanical

stirrer was used to mix the reactants. The low temperatures required for the reactions were maintained by immersion of the reaction vessel into a 5 L Dewar containing a liquid nitrogen-pentane slush bath. The temperature of the reaction mixture could be manipulated by raising or lowering the Dewar with a mechanical jack. In this way it was possible to vary the temperature over a range of -30°C to -90°C required for this synthesis.

Synthesis of 6,6'-Dibromo-2,2'-bipyridine

Typically, 250 mL of dry and freshly distilled ethyl ether was added to 25.0 g (0.106 mmol) of 2,6-dibromopyridine. The resulting white sulrry was cooled to below -60°C. An equivalent amount of n-butyl lighium (0.106 mmol) was added dropwise to the slurry while maintaining the temperature below -60°C. A clear, yellowish-green solution resulted. The solution was stirred for an additional 60 min after addition was completed. At this time the solution was warmed to -40°C for 10 min and then recooled to -90°C. It often required the pouring of liquid nitrogen directly over the reaction vessel to achieve this temperature in a reasonable length of time. When this temperature was reached, 9.09 g of anhydrous $CuCl_2$ (0.053 mmol) was added. The resulting brownish mixture was strongly stirred for one hour while the temperature was kept below -60°C. At the end of one hour, compressed air, passed through a drying tube containing P_5O_{10} and $CaCl_2$, was bubbled through the system

overnight. The air was purged from the system with nitrogen and 100 mL of 6N HCl added. The resulting greenish-brown mixture was filtered, and a brown solid was collected. This solid was washed several times with one normal HCl solution to remove the brown color which was presumed to be due to the presence of Cu(II) ions. The remaining solid was recrystallized from toluene until the melting point matched the published values for 6,6'-dibromo-2,2'-bipyridine of 221-223°C.[24]

The ether and water layers were separated. The ether layer was evaporated to dryness, and the resulting tan solid was collected. The water layer was neutralized with a saturated solution of $NaHCO_3$. The neutralized solution was extracted with toluene in a 500 mL separatory funnel. Extraction was continued until no color was observed in the toluene layer. The water layer was then discarded. The toluene extracts were combined and evaporated to dryness. The solid collected was combined with the solid from the ether layer. The combined solid was recrystallized from toluene. The yields for this synthesis were poor and never exceeded 25% based on the amount of 2,6-dibromopyridine used. The published yield for this synthesis was 50%.[24] The 6,6'-dibromo-2,2'-bipyridine thus produced was used in the next step to synthesize 6,6'-diformyl-2,2'-bipyridine.

Synthesis of 6,6'-Diformyl-2,2'-bipyridine

Typically, 5 g (115.9 mmol) of 6,6'-dibromo-2,2'-bipyridine was used in this step. The dibromobipyridine was dissolved in 150 mL of warm THF in a septum covered erlenmeyer flask. A nitrogen atmosphere was maintained over the solution. This warmed solution was transferred via syringe to the 250 mL addition funnel. The solution was slowly added to the reaction flask containing 31.8 mM of n-butyl lithium in 100 mL of THF that was previously cooled to below -80°C. The rate of addition of the dibromobipyridine-THF solution was slow enough so that the temperature of the reaction solution was maintained below -70°C but rapid enough so that little solid collected on the spout of the funnel. Upon addition of the dibromobipyridine solution, the pale yellow n-butyl lithium solution turned a faint orange color and, finally, a deep red color. After addition was complete, the reaction solution was stirred for one hour. After one hour 5 mL of N,N-dimethylformamide in 50 mL of THF was added dropwise. The reaction solution immediately turned a deep purple color. The solution was stirred for one hour after addition was complete. It was then allowed to warm to -30°C. Addition of 50 mL of 4 N HCl resulted in a clear, two-phase solution. The violet upper layer was separated from the orange lower layer in a separatory funnel. The upper layer was evaporated to dryness and the reddish solid collected. The lower layer was neutralized with saturated $NaHCO_3$ solution and extracted with toluene. The toluene extract

was evaporated to dryness. The two solids were combined and washed with methanol and recrystallized from toluene. The 6,6'-diformyl-2,2'-bipyridine had a melting point of 235°C and showed a strong IR absorption band at 1710 cm^{-1}. The yield for this reaction was superior to the previous reaction and ranged from 50-70% based on starting dibromobipyridine.

Synthesis of 6,6'-Diformyl-2,2'-bipyridinebissemicarbazone (DFBPSC)

Two grams (9.4 mmol) of 6,6'-diformyl-2,2'-bipyridine was added to 100 mL of 95% ethanol. To this solution, 2.1 g (18.9 mmol) of semicarbazide hydrochloride (SCA·HCl) was added with 25 mL of H_2O. After stirring for one hour, the yellow mixture was neutralized with $NaAc \cdot 3H_2O$ (2.57 g, 18.9 mmol). The yellowish mixture was filtered. The yellow solid was washed with H_2O and technical grade ethyl ether. The resulting whitish solid decomposed without melting above 275°C. The DFBPSC was used as needed with a variety of metal salts.

Synthesis of $M^{+n}(DFBPSC)(NO_3)_n$

Equimolar amounts of DFBPSC and the nitrate salt of the metal were mixed in a 3:1 ratio of water to ethyl alcohol. The resulting yellowish mixture was stirred and heated for one hour. Additional water was added to enhance solubility. A small amount of solid did not dissolve. This solid was removed by filtration. The solution was allowed to evaporate slowly at room temperature. Crystals formed within a

few days. The crystals of the europium compound were found to decompose after a few weeks. This decomposition was accelerated under the X-ray beam. Fresh crystals of this compound were obtained by redissolution of the decomposed crystals in water and subsequent slow evaporation.

The density of the crystals was determined by the flotation method. The density of the flotation liquid for the La, Eu and the phthalazine compounds was measured with a hygrometer. The density of the flotation liquid for the Hg compound was outside the range of the hygrometers available. Its density was determined by weighing an accurately known volume of the flotation liquid.

Infrared Spectra

Infrared spectra were obtained from a Perkin-Elmer 283B spectrophotometer. All spectra were obtained from Nujol emulsions on sodium chloride plates. The spectra were calibrated using the 1601 cm^{-1} absorption from a polystyrene film. A list of the ligand and metal complex absorption frequencies is located in Table I.

A number of changes in the spectra of the ligand can observed upon complexation with a metal ion. The doublet at 3500 cm^{-1} and 3450 cm^{-1} characteristic of the N-H stretch of the amide group is considerably broadened.[25] This effect is also noted for the DAPSC complexes.[26] The absorption band due to the carbonyl stretch appears at 1710 cm^{-1} in the uncomplexed ligand. This is at a slightly higher resonance

Table I

Infrared Spectra*

DFBPSC	Eu(DFBPSC)-$(NO_3)_3 \cdot 2H_2O$	La(DFBPSC)-$(NO_3)_3 \cdot 3H_2O$	[Hg(DFBPSC)-$(NO_3)_2]_2$
	3550(b)	3600(b)	
3480(m)	3380(b)	3450(b)	3400-3150(b)
3430(m)	3300-3200(b)	3350-3200(b)	
1710(s,b)	1700(s,b)	1700(m)	1670(s,b)
1650(w)	1680(s,b)	1670(s)	
1605(s,b)	1635(m)	1625(m)	1610(w)
1570(s)	1575(s)	1575(s)	
1530(w)	1550(s)	1500(s)	1540(s,b)
1330(m)	1350(m)	1330(b)	1310(w)
1280(w)	1290(m,b)		1280(m)
1250(w)		1230(w)	1240(m)
1170(m)	1190(m)	1190(w)	1180(m,b)
	1160(s)	1160(s)	1140(w)
1110(w)	1120(m,b)	1110(w)	
1090(w)			
180(w)			
	1030	1040	1040
1010	1005	1000	1010
990	980		960
935	940	950	940
			920
860			
830	830	820	
800	805	810	810
	740	730	730

*Each column contains absorption peaks (cm^{-1}) and the relative intensity (s, strong; m, medium; w, weak; b, broad).

than that reported for similar species.[27] Upon complexation the absorption is shifted to a lower frequency. In the case of the Eu and La compounds this band is split into two resonances. Broadened absorption bands due to lattice water appear at 3500 cm^{-1} in the Eu and La compounds.[28] It is difficult to determine the mode of binding of the nitrate ions from the spectra due to interference from the ligand and the Nujol.

Diffraction Experiments

Preliminary space group and cell constants were determined from photographs taken on a Buerger precession camera.[29] All intensity measurements were made on a Syntex $P\bar{1}$ diffractometer. Coordinates for 15 intense reflections were obtained from a Polaroid picture taken with a cassette camera mounted on the diffractometer. These reflections were centered and preliminary values for axial lengths and interaxial angles were calculated. A cell was chosen based on agreement of these values with those obtained from the precession photographs. A least-squares fit of 2θ, ω, ϕ and χ settings for each reflection yielded accurate cell constants and estimated standard deviations. Ultimately it was the acceptability of these values that determined whether the experiment was continued or the crystal was discarded and a new crystal mounted.

Once a suitable crystal was found and the cell dimensions determined, intensities for symmetry independent

reflections were measured and recorded on a magnetic tape. Four standard reflections were remeasured every 96 reflections to monitor the stability of the crystal and x-ray source. The intensities of all reflections were scaled based on the initial sum of the intensities of these four standard reflections. Any duplicate reflections were averaged. Molybdenum radiation was used in all cases. A low order reflection from a graphite crystal was used as a source of monochromatic radiation.

A θ-2θ variable speed scan technique[30] was employed in the data collection except where noted. The scan rate was determined on the basis of a 2 sec prescan of the reflection to be measured. The scan rate was varied linearly from 1°/min for counts of 150 or less to 25°/min for counts of 1500 or more. The intensity of a reflection is given by

$$\text{Intensity} = \text{scan rate}\left(\text{total scan counts} - \frac{\text{background counts}}{\text{background-to-scan-time ratio}}\right) .$$

The background was measured at the limits of each reflection, and the background-to-scan-time ratio was always 1:2. The estimated standard deviation, $\sigma(I)$, was calculated for each reflection and is given by

$$\sigma(I) = \left(\text{total scan counts} + \frac{(\text{background count})^2}{\text{background-to-scan-time ratio}}\right)^{\frac{1}{2}} .$$

Reflections were considered absent if the intensity of the reflection was less than $2\sigma(I)$ times the background

intensity. These reflections were not used in subsequent calculations. The raw intensity data were sorted for convenience of inspection of the data. These sorted data were examined to determine if the space group based on the precession photographs was consistent with these observed reflections. The intensities were corrected for Lorentz and polarization effects of the form

$$\frac{1}{Lp} = \frac{\sin 2\theta}{(1 + \cos^2 2\theta)} .$$

An initial scale factor and an estimate of the isotropic temperature factor were obtained from a Wilson plot.[31] When a question arose as to whether or not a center of symmetry was present in the crystal recourse was made to the intensity distribution method suggested by Wilson[32] and the N(z) test of Howells et al.[33] Pertinent crystallographic data for the compounds used in this study are found in Table II.

The ultimate aim of any crystallographic experiment is the calculation of an electron density map of the unit cell. Atomic positions are inferred from the regions of highest electron density. The electron density can be calculated from the following equation:[34]

$$\rho(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_\ell F_{hk\ell} \, e^{-2\pi i(hx+ky+\ell z)} ,$$

where $\rho(x,y,z)$ is the electron density at the point x,y,z in the unit cell, and $F_{hk\ell}$ is the structure factor for the reflection hkℓ. The structure factor is a quantity that is

Table II

Crystallographic Data

Compound	$Eu(DFBPSC)(NO_3)_3 \cdot 2H_2O$
Crystal System	Monoclinic
Space Group	$P2_1/n$
a(Å)	21.903(5)
b(Å)	15.478(6)
c(Å)	7.767(3)
α(°)	90*
β(°)	93.75
γ(°)	90*
Volume ($Å^3$)	2627(2)
Mol Wt (g/mol)	700.30
z	4
$Density_{(meas)}$ (g/cc)	1.82
$Density_{(calc)}$ (g/cc)	1.77

* Required by Crystal System to be equal to 90°.

Table II--extended

$La(DFBPSC)(NO_3)_3 \cdot 3H_2O$	$(Hg(I)(FBPSC(NO_3)_2)_2$	$DHPHPY \cdot 3H_2O$
Triclinic	Orthorhombic	Monoclinic
$P\bar{1}$	Fddd	$P2_1/c$
8.230(4)	23.291(11)	9.407(2)
11.833(7)	22.611(15)	15.082(3)
13.805(5)	14.954(9)	14.617(3)
75.78(4)	90*	90*
88.40(4)	90*	96.95(2)
89.87(5)	90*	90*
1302(1)	7876(8)	2858(1)
704.97	1301.85	422.45
2	8	4
1.85	2.21	1.36
1.80	2.20	1.36

related to the scattering power of all the atoms in the unit cell. The structure factor is related to the individual scattering factors of the atoms by the relations,[34]

$$F_{hk\ell} = \sum_j f_j \, e^{2\pi i\alpha} ,$$

where f_j is the scattering factor for the jth atom, and $2\pi i\alpha$ is the phase angle contribution of that atom. The scattering factors were obtained from the International Tables for X-ray Crystallography.[35] Corrections for anomolous dispersion effects were applied to the metal atoms only and not until the least-squares refinemcnt stage. The structure factor, $F_{hk\ell}$, is not a directly observable quantity. The structure factor amplitude, $|F_{hk\ell}|$, or, as it is sometimes written, $|F_{obs}|$, can be derived from the measured intensities, but the phase information is lost. The relationship between the structure factor and the structure factor amplitude is given below:[34]

$$F_{hk\ell} = |F_{hk\ell}| \, e^{2\pi i\alpha(hk\ell)} .$$

Incorporating this relationship into the equation for the electron density yields the following equation:[34]

$$\rho(x,y,z) = \frac{1}{V} \sum\sum\sum_{hk\ell} |F_{hk\ell}| \, e^{-2\pi i(hx+ky+\ell z-\alpha)} .$$

The derivation of the value for α for each reflection constitutes the phase problem in crystallography.

There are two basic approaches that we use in this lab to solve the phase problem. If there is one atom or more in the compound under study whose scattering factors are significantly greater than those of the rest of the atoms, than the position of these atoms can be located by the use of the Patterson function. This function is similar to the one used to calculate the electron density and is shown below:[34]

$$P(u,v,w) = \frac{1}{V} \sum_{hk\ell} \sum \sum |F_{hk\ell}|^2 \cos 2\pi(hx+ky+\ell z) \ .$$

The resulting map can be interpreted in terms of interatomic vectors. A peak located at point u,v,w in the Patterson map means there are atoms located at x_1,y_1,z_1 and x_2,y_2,z_2 such that

$$u = x_2 - x_1$$
$$v = y_2 - y_1$$
$$w = z_2 - z_1 \ .$$

The height of each peak is proportional to the product of the atomic numbers of the atoms involved. The vector peak resulting from the heavy atom-heavy atom vector will usually be the largest peak in the map. Therefore the heavy atom can be located in the cell and its contribution to the phase $2\pi\alpha_{hk\ell}$ calculated. It can be seen from the form of the equation for the structure factor that the contribution of the heavy atom will tend to dominate the scattering. An electron density map is calculated based on the observed structure

factor amplitudes, $|F_{obs}|$, and the phase contribution of the heavy atom. The resulting map will frequently reveal the presence of other atoms in the compound. The phase contribution of these new atoms is combined with that of the heavy atom and a new electron density map is calculated. This map will reveal more of the structure and even better phase information is obtained. This cyclic process is continued until all the non-hydrogen atoms have been located. When this stage has been reached, the refinement process can begin.

For complicated structures that do not contain a heavy atom, the Patterson map is very often uninterpretable. To obtain a phasing model for such light atom structures we utilize a package of direct methods programs known as MULTAN 78.[36] Direct methods can be differentiated from other methods such as the heavy atom method in that no prior knowledge of atomic positions is necessary in determining phases for a set of structure factors. In direct methods, phases are determined on a statistical basis. Early uses of these methods were limited to centrosymmetric space groups since in these space groups phase values are limited to 0 or π. This is equivalent to assigning a plus or minus sign to a structure factor amplitude. With the advent of low cost, high speed computing the more difficult problem of an acentric structure can be solved more or less routinely.

The first step in the MULTAN program is the conversion of the $|F_{hk\ell}|$ data to normalized structure factors, $|E_{hk\ell}|$,

as proposed by Karle and Hauptman.[37] The conversion is given by

$$|E_{hk\ell}|^2 = \frac{|F_{hk\ell}|^2}{\varepsilon \Sigma f_j^2(B)} ,$$

where B is the temperature factor obtained from a Wilson plot, and ε is an integer to account for space group symmetry elements. This effectively puts all the reflections on a common basis.

A number of the largest E values are kept, usually 7 to 10 per atom in the asymmetric unit. From this list reflections whose indices are related such that for a pair of reflections h and h' there exists a third reflection h-h' are determined. Such reflections are known as Σ_2 triplets. From the reflections with the largest E values that enter into the greatest number of such interactions enough phases are assigned to define the origin and enantiomorph if necessary. Indications for phases for additional reflections are based on these first few reflections.

For an equal atom, centrosymmetric structure, the probability that the sign for a reflection h is positive is given by[38]

$$P_+(h) = \tfrac{1}{2} + \tfrac{1}{2}\tanh\left(\frac{1}{\sqrt{N}}|E_h| \sum_{h'} E_{h'} E_{h-h'}\right) ,$$

where N is the number of atoms in the unit cell, and the summation term represents all the reflections that enter into Σ_2 triplets with the reflection h.

For acentric structures phase values can range from 0 to 2π. A numerical value of the phase ϕ for the reflection h is estimated by use of a modified version of the tangent formula of Karle and Hauptman which is shown below:[39]

$$\tan \phi_h = \frac{\Sigma\, w_{h'} w_{h-h'} |E_{h'} E_{h-h'}| \sin (\phi_{h'} + \phi_{h-h'})}{\Sigma\, w_{h'} w_{h-h'} |E_{h'} E_{h-h'}| \cos (\phi_{h'} + \phi_{h-h'})},$$

where $w_{h'}$ and $w_{h-h'}$ are weights associated with the reflections h' and h-h'. The main drawback of these two methods is that they start with only a few reflections of known phase and use these to give phase indications for enough reflections to get a recognizable Fourier map. This process has been likened to building a pyramid upside down.[34] However once a set of phases has been developed, an electron density map is calculated based on the normalized structure factors.[40] Often most of the non-hydrogen atoms can be located from this E map. Once these atoms are located cyclic Fourier syntheses can be commenced using all the observed structure factor amplitudes. Any non-hydrogen atoms not located from the E map can now be located if the phasing model is correct.

To estimate how the trial structure compares to the actual structure, a reliability index, R, is calculated after each Fourier routine and after each stage in the refinement process. The R value is defined as

$$R = \frac{\Sigma||F_{obs}|-|F_{calc}||}{\Sigma|F_{obs}|} .$$

It is often given as a percentage. The lower the R value the better the agreement between $|F_{obs}|$ and $|F_{calc}|$ and, presumably, the better the model.

Once all non-hydrogen atoms have been located the trial structure is refined by least-squares minimization of the function

$$\text{Residual} = \Sigma\, w(||F_{obs}| - |F_{calc}||)^2 ,$$

where w is a weighting term equal to $1/\sigma^2$. Initially isotropic temperature factors are used for all atoms. Finally, anisotropic temperature factors are applied. After three cycles of anisotropic least-squares routines, a difference Fourier map is calculated to locate the hydrogen atoms in the compound. This difference Fourier synthesis may be expressed in the form[34]

$$\Delta\rho = \frac{1}{V} \Sigma\Sigma\Sigma_{hk\ell} (|F_{obs}| - |F_{calc}|)\, e^{-2\pi i(hx+ky+\ell z-\alpha_c)} ,$$

where α_c is the phase of $|F_{calc}|$. The hydrogen atoms are arbitrarily assigned isotropic temperature parameters. The hydrogen parameters are used in but not refined during the final three cycles of anisotropic least-squares refinement.

The programs used for all calculations were either written or modified to be compatible with existing programs by Dr. G. J. Palenik.

CHAPTER TWO

DISCUSSION OF METAL COMPLEXES OF 6,6'-DIFORMYL-2,2'-BIPYRIDYLBISSEMICARBAZONE

Complexes of DFBPSC were prepared by direct reaction of the ligand with the nitrate salt of the metal in a water-ethanol solution. Crystals formed within a few days. These crystals were used in the X-ray experiment. The results of such experiments are the subject of this chapter.

Structural Solution and Refinement for $(Hg(DFBPSC)(NO_3)_2)_2$

The space group of $(Hg(DFBPSC)(NO_3)_2)_2$ was uniquely determined from the systematically absent reflections as revealed from the precession photographs. The space group was found to be Fddd. From the measured density and volume of the cell, there were calculated to be 16 Hg atoms in a unit cell which requires that the Hg atoms be located on one of the five special positions.[35] A Patterson map was calculated, and it revealed a large peak at $u,\frac{1}{4},\frac{1}{4}$. This peak was interpreted to be a Hg-Hg vector. The position of the Hg atom was thus located and was used as a phasing model for a Fourier synthesis. All 17 atoms in the asymmetric unit were located in three Fourier cycles. The R value at this stage of refinement was 16.0%. Three cycles of least-squares refinement with isotropic thermal parameters for all atoms

lowered the R value to 9.8%. Three more least-squares cycles with anisotropic thermal parameters for the Hg atom only lowered the R to 6.2%. Finally all the atoms were treated anisotropically, and after three additional cycles of least-squares, a final R value of 5.9% resulted. A difference Fourier was calculated and revealed no large peaks and sensible positions for only three of the possible seven H atoms in the asymmetric unit. These H atom positions were not used, and no subsequent refinement was deemed necessary.

Structural Solution and Refinement for La(DFBPSC)$(NO_3)_3 \cdot 3H_2O$

Precession photographs on the La(DFBPSC)$(NO_3)_3 \cdot 3H_2O$ showed no obvious symmetry axes nor any systematically absent reflections. These observations were corroborated from data obtained from a similar crystal that was mounted on the diffractometer. The space group for this compound was therefore either P1 or $P\bar{1}$. Because the results of the intensity statistics tests indicated an acentric distribution of atoms, the space group was initially chosen to be P1. This required that two molecules be located in the unit cell. The positions of the two La atoms were located using the MULTAN programs. However, after a series of Fourier calculations located the full coordination sphere of both La atoms and all the atoms in the two ligands, it was apparent that these two groups of atoms were related by a center of symmetry. The origin of the unit cell and the positions of one group of atoms were transformed to reflect the presence of a center.

Cyclic Fourier analysis on the centric structure revealed all 40 atoms in the molecule. Isotropic least-squares refinement lowered the R value to 8.7%. Three cycles of anisotropic least-squares refinement lowered the R to 6.1%. A difference Fourier map revealed 19 out of 20 H atom positions. The H atom positions were included in, but not refined during, the final six cycles of least-squares refinement. The final R value was 5.6%.

Structural Solution and Refinement for $Eu(DFBPSC)(NO_3)_3 \cdot 2H_2O$

The crystal system of the $Eu(DFBPSC)(NO_3) \cdot 2H_2O$ was shown to be monoclinic from the precession photographs. The systematically absent reflections indicated that the space group was $P2_1/n$. This compound decomposed on the diffractometer after a couple of days as was noted by the drastic fallcff in intensity of the standard reflections. This was not long enough for a complete sct of data to be collected using the variable speed scan technique. A new crystal was mounted and a data set was collected using a constant scan rate of 12°/min.

The position of the Eu atom was also lccated using the MULTAN programs. The position of the Eu atom was used as a phasing model for subsequent Fourier syntheses. A series of Fourier maps revealed the positions of the atoms in the ligand and the three nitrate ions. The structure was refined in the manner described for the Hg and La compounds. A

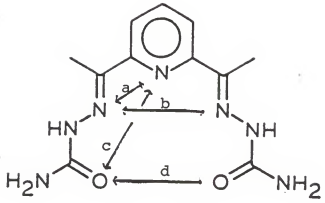
difference Fourier map revealed the positions of 10 of the 20 H atoms. These atoms were assigned isotropic thermal parameters and used in, but not refined during, the six final cycles of least-squares. An R value of 8.1% was calculated at this stage. A comparison of the measured density (1.85 g/cc) and the density calculated based on a formula $Eu(DFBPSC)(NO_3)_3$ (1.68 g/cc) indicated some additional atoms remained to be found. A difference Fourier was calculated with atom C(14) left out. This was done as a scaling aid. The peak due to atom C(14) could be compared to other peaks in the electron density map. A number of peaks stood out above the general background but were all smaller than the peak due to atom C(14). These were attributed to the presence of water molecules on the basis of the IR spectra. The size of the peaks indicated that these molecules were disordered.[34] No attempt was made to calculate an occupancy factor. The four largest peaks were half weighted in subsequent Fourier and least-squares calculations. The chemical formula for this compound was then taken to be $Eu(DFBPSC)(NO_3)_3 \cdot 2H_2O$. The final R value was calculated to be 6.1%.

Results and Discussion

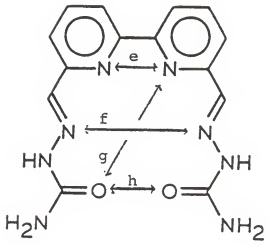
At the outset of this work it was proposed that DFBPSC would serve as a useful ligand in the synthesis of HBP complexes much as DAPSC was in the synthesis of PBP complexes. The two ligands are quite similar but at the same time they have some very important differences. The use of

6,6'-diformyl-2,2'-bipyridine in the condensation reaction with SCA·HCl creates a cavity that is larger than that formed in the same reaction with DAP. The first row transition metals provided a good fit to the cavity in DAPSC, but these metal ions are too small to utilize effectively all six donors in DFBPSC. For example, using both the hexadentate ligands 6,6'-diacetyl-2,2'-bipyridylbissemicarbazone (DAPBSC)[41] and its phenanthroline analogue PHENSC[42] with $Co(NO_3)_2$ results in a seven coordinate species with the N(12)-N(13) bond of the semicarbazone sidearm rotated so that the carbonyl oxygen of that group was no longer in position to coordinate to the metal. Figure 3 shows the ligand DAPSC and the ligand DFBPSC, and Table III lists some of the pertinent distances between donor atoms of the two ligands. These distances were calculated based on the simplifying assumption that all bond lengths were 1.4 Å and all bond angles were 120°. Both ligands were also assumed to be planar. Because of the larger cavity of DFBPSC and the results with Co(II), a move to some larger metal ions was necessitated.

The lanthanides were chosen because of the large size of their +3 ions[43] and because relatively little work has been done with these ions. Crystal structure determinations of Y and some lanthanides with DAPSC[26] indicated that these ions did not quite fit into the cavity formed by the ligand. Preliminary calculations indicated that DFBPSC should provide a suitable cavity for these ions.



DAPSC



DFBPSC

Figure 3

Comparison of DAPSC and DFBPSC

Table III

Interatomic Distances between Donor Atoms in Idealized Planar Ligands DAPSC and DFBPSC

	DAPSC		DFBPSC
a	2.80 Å	e	2.80 Å
b	4.85 Å	f	5.60 Å
c	4.85 Å	g	5.60 Å
d	4.85 Å	h	2.80 Å

La(III) and Eu(III) have 4f orbital configurations of $4f^0$ and $4f^6$, respectively. Using the values for the crystal radius for the +3 oxidation state supplied by Shannon[43] for these two ions for a variety of coordination numbers indicates that La(III) is about 0.09 Å larger than Eu(III). This difference is due to the well-known lanthanide contraction. The chemistry of the lanthanides is similar to that of the alkaline earth metal ions.[44,45] They are both considered to be hard acids.[46] Because of their similarities, Ln(III) ions can be used to replace Ca(II) ions in molecules of biological interest as NMR shift reagents[47] and as luminescence probes.[48]

In addition to the La(III) and Eu(III) ions, the complexation of DFBPSC to Hg(II) was also studied. The crystal radii of La(III) and Hg(II) for coordination numbers six and eight[43] indicate that these two ions are about the same size. Moreover, Hg(II) should offer a very interesting contrast to the Ln(III) ions as the chemistry of Hg(II) is quite different from that of the lanthanides. Hg(II) is considered a soft acid.[46] Hg(II) forms organometallic compounds that are stable to air and water. For example, diphenyl mercury can be synthesized from phenyl mercuric bromide and excess sodium cyanide in a water solution.[49] By contrast the organolanthanides are all either air or water sensitive.[50,51] The chlorides, bromides and iodides of Hg(II) are all covalent compounds whereas those of the Ln(III) ions are ionic. In addition, typical coordination for Hg(II) is two or four[52] with a few six coordinate species known while that of the

lanthanides is usually much higher.[45] There are also no known examples of Hg(II) exhibiting HBP geometry. With the larger Ln(III) and Hg(II) ions, the donor atoms of DFBPSC should be effectively utilized, and the difference in chemistry of these ions makes their choice an interesting one.

In addition to the size differential between DAPSC and DFBPSC, the latter ligand has some additional flexibility in that rotation about the carbon-carbon bond joining the two pyridine rings to form bipyridyl is also possible. The X-ray structure of the molecule 2,2'-bipyridine was done some time ago.[53] The uncomplexed molecule is completely planar with the nitrogen atoms trans relative to each other. Upon complexation the nitrogens are in the cis position so both may coordinate to the metal ion. However, in the coordinated complex the bipyridyl group is not found to be planar in the general case.[54-70] This deviation from planarity is most likely due to steric interaction between the hydrogen atoms in the 3 and 3' positions. The magnitude of the dihedral angle between the two pyridine rings in these bipyridal complexes is variable. The range extends from an essentially planar bipyridyl group[54,55] to one having a dihedral angle of 31°.[56] This effect would not seem to be correlated to metal ion size or type as the extreme examples[54-56] were reported for Cu(II) complexes. With DFBPSC an interesting effect can be related to the magnitude of the dihedral angle. As the dihedral angle increases, the size of the cavity formed by the six donor atoms in the ligand increases. On strictly an

ion size basis, it might be expected that this angle will be larger for the La(III) compound than for the Eu(III) compound and about the same as that for the Hg(II) compound.

The results of the structure determination for the three compounds are quite interesting. All donor-to-metal distances are listed in Table IV. The comparative bond distances and angles for the ligand in the three complexes are listed in Tables V and VI, respectively. The final positional and thermal parameters for these compounds are listed in Tables VII through XII.

The La(III) compound is found to be an eleven coordinate structure. This is an uncommon coordination number.[1,3] The La(III) ion is coordinated by the six donors of the ligand, two bidentate nitrate ions, and one water molecule. An ORTEP drawing[71] of the compound is shown in Figure 4. The average donor-to-metal bond distance for the compound is 2.68 Å. This value is comparable to the average bond distances of 2.66 Å for $La(NO_3)_3 \cdot 5H_2O$[72] and 2.65 Å for $La(DAPBAH)(NO_3)_3$,[11] both eleven coordinate species. The Eu(III) complex is found to be ten coordinate with two bidentate nitrate ions in addition to the six donors of the ligand. An ORTEP[71] of the Eu compound is shown in Figure 5. The average donor-to-metal bond distance for this compound is 2.53 Å which is quite close to the value of 2.57 Å which is the average bond distance for the only other ten coordinate Eu(III) complex characterized by X-ray methods.[73] It is interesting to note that the difference in average bond distances between the La(III) and the Eu(III) DFBPSC

Figure 4

ORTEP Drawing and Atomic Numbering Scheme for
$La(DFBPSC)(NO_3)_3 \cdot 3H_2O$

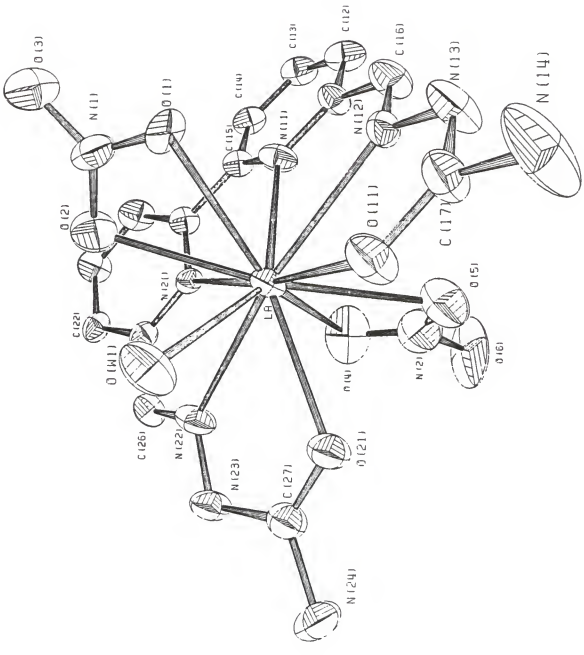

O(3)
N(1)
O(1)
C(15)
C(14)
C(13)
C(12)
C(16)
N(13)
N(14)
O(2)
N(11)
N(12)
O(11)
C(17)
O(12)
N(21)
Eu
O(15)
C(22)
O(14)
N(2)
O(16)
O(13)
C(26)
N(22)
O(21)
N(23)
C(27)
N(24)

Figure 5

ORTEP Drawing and Atomic Numbering Scheme for
$Eu(DFBPSC)(NO_3)_3 \cdot 2H_2O$

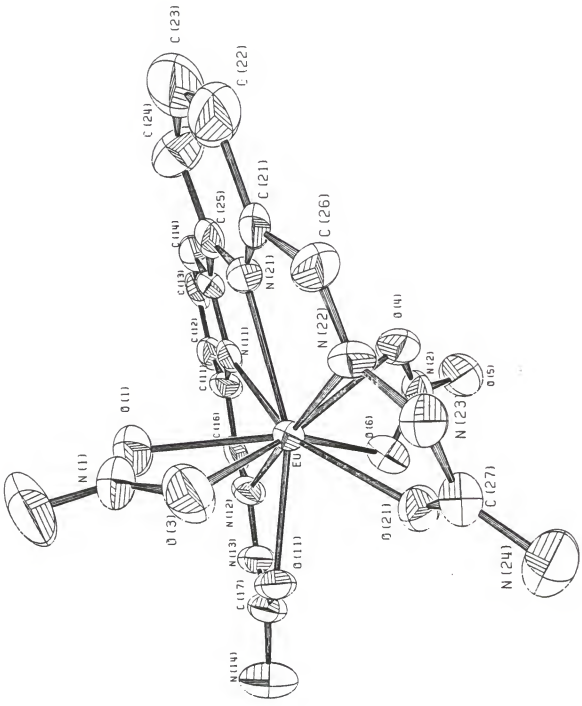

C(23)
C(22)
C(24)
C(21)
C(25)
C(26)
C(14)
C(13)
N(21)
C(12)
N(11)
N(22)
O(14)
C(11)
N(2)
O(15)
O(1)
C(16)
O(6)
N(23)
EU
N(1)
O(3)
N(12)
O(21)
C(27)
N(13)
O(11)
C(17)
N(24)
N(14)

Table IV

Metal-to-Donor Atom Distances
for Complexes of DFBPSC

	Eu	La	Hg
N(11)	2.638(14)	2.788(10)	2.385(18)
N(12)	2.594(14)	2.732(10)	2.268(18)
O(11)	2.449(10)	2.589(9)	2.485(18)
N(21)	2.609(13)	2.810(9)	*
N(22)	2.597(13)	2.707(10)	*
O(21)	2.442(10)	2.564(8)	*
O(1)	2.477(13)	2.649(9)	
O(2)		2.687(10)	
O(3)	2.520(13)		
O(4)	2.495(12)	2.619(13)	
O(5)		2.710(12)	
O(6)	2.503(12)		
O(w1)		2.574(9)	

*Required by symmetry to be equal to distance for analogous donor atom in first half of ligand.

Table V

Ligand Bond Distances for
Metal Complexes of DFBPSC

	La	Eu	Hg
C(11)-N(11)	1.364(16)	1.349(22)	1.338(28)
C(11)-C(16)	1.439(18)	1.427(22)	1.466(33)
C(11)-C(12)	1.390(18)	1.370(23)	1.403(34)
C(12)-C(13)	1.388(20	1.329(24)	1.396(38)
C(13)-C(14)	1.373(18)	1.392(29)	1.409(31)
C(14)-C(15)	1.389(18)	1.409(23)	1.407(33)
C(15)-N(11)	1.340(15)	1.346(20)	1.321(28)
C(15)-C(25)	1.478(17)	1.520(26)	1.504(29)
C(16)-N(12)	1.284(17)	1.283(22)	1.286(28)
N(12)-N(13)	1.357(15)	1.343(19)	1.358(27)
N(13)-C(17)	1.348(17)	1.362(23)	1.378(33)
C(17)-O(11)	1.236(16)	1.265(21)	1.287(31)
C(17)-N(14)	1.325(19)	1.281(24)	1.352(34)
C(21)-N(21)	1.332(15)	1.293(22)	*
C(21)-C(26)	1.449(17)	1.426(23)	*
C(21)-C(22)	1.396(16)	1.454(26)	*
C(22)-C(23)	1.401(18)	1.325(28)	*
C(23)-C(24)	1.379(21)	1.385(32)	*
C(24)-C(25)	1.395(18)	1.364(26)	*
C(25)-N(21)	1.332(15)	1.335(20)	*
C(25)-C(15)	1.478(17)	1.520(26)	*
C(26)-N(22)	1.268(17)	1.252(22)	*
N(22)-N(23)	1.377(15)	1.358(18)	*
N(23)-C(27)	1.380(16)	1.334(23)	*
C(27)-O(21)	1.236(16)	1.207(21)	*
C(27)-N(24)	1.338(18)	1.362(24)	*

*Required by symmetry to be equal to values found for analogous atoms in first half of ligand

Table VI

Ligand Bond Angles for
Metal Complexes of DFBPSC

	La	Eu	Hg
N(11)-C(11)-C(16)	117.5(11)	115.0(14)	116.7(20)
N(11)-C(11)-C(12)	123.4(11)	122.5(15)	123.1(21)
C(12)-C(11)-C(16)	119.0(11)	122.2(16)	120.2(21)
C(11)-C(12)-C(13)	117.7(12)	121.3(17)	118.0(22)
C(12)-C(13)-C(14)	119.3(12)	118.8(16)	119.2(22)
C(13)-C(14)-C(15)	120.1(12)	117.4(16)	117.2(21)
N(11)-C(15)-C(14)	121.9(11)	122.9(15)	124.0(21)
N(11)-C(15)-C(25)	116.5(10)	114.4(14)	116.4(19)
C(14)-C(15)-C(25)	121.6(11)	122.6(15)	119.6(20)
C(11)-N(11)-C(15)	117.5(10)	116.6(13)	118.2(19)
N(12)-C(16)-C(11)	120.6(12)	119.1(16)	118.1(20)
N(13)-N912)-C(16)	118.8(11)	121.9(14)	119.5(18)
N(12)-N(13)-C(17)	115.6(11)	119.1(14)	116.6(19)
O(11)-C(17)-N(13)	121.8(12)	116.2(15)	121.2(23)
O(11)-C(17)-N(14)	123.3(13)	124.9(17)	121.0(24)
N(13)-C(17)-N(14)	114.9(12)	118.8(16)	117.8(24)
N(21)-C(21)-C(26)	118.4(10)	120.1(15)	*
N(21)-C(21)-C(22)	122.4(11)	122.2(16)	*
C(22)-C(21)-C(26)	119.2(11)	118.6(16)	*
C(21)-C(22)-C(23)	119.0(12)	119.0(18)	*
C(22)-C(23)-C(24)	117.4(13)	118.3(20)	*
C(23)-C(24)-C(25)	120.4(13)	120.1(19)	*
N(21)-C(25)-C(24)	121.5(11)	122.1(16)	*
N(21)-C(25)-C(15)	117.3(10)	117.8(14)	*
C(24)-C(25)-C(15)	121.2(11)	120.0(16)	*
C(21)-N(21)-C(25)	119.2(10)	119.0(14)	*
N(22)-C(26)-C(21)	117.1(11)	115.6(16)	*
N(23)-N(22)-C(26)	118.2(11)	120.9(14)	*
N(22)-N(23)-C(27)	115.0(10)	113.4(14)	*
O(21)-C(27)-N(23)	120.9(11)	124.0(16)	*
O(21)-C(27)-N(24)	123.1(12)	122.6(17)	*
N(23)-C(27)-N(24)	116.1(12)	113.3(16)	*

*Required by symmetry to be equal to angles for analogous atoms in first half of ligand.

Table VII

Final Positional Parameters for Non-hydrogen Atoms in $Eu(DFBPSC)(NO_3)_3 \cdot 2H_2O$[a]

ATOM	X	Y	Z
EU	50855(4)	23459(6)	25809(13)
C(11)	4003(11)	3875(14)	995(29)
C(12)	3677(12)	4625(16)	733(31)
C(13)	3935(12)	5397(15)	1323(28)
C(14)	4511(13)	5397(14)	2040(31)
C(15)	4823(11)	4602(13)	2292(27)
C(16)	3783(12)	3065(16)	312(27)
C(17)	4332(11)	967(14)	-20(28)
C(11)	4822(7)	1070(9)	820(19)
N(11)	4568(9)	3838(11)	1795(22)
N(12)	4126(9)	2396(11)	505(20)
N(13)	3941(9)	1623(12)	-166(25)
N(14)	4197(10)	240(14)	-796(31)
C(21)	6199(12)	3709(15)	4310(28)
C(22)	6619(13)	4428(17)	4699(36)
C(23)	6398(15)	5213(19)	4264(39)
C(24)	5813(12)	5290(16)	3480(37)
C(25)	5479(11)	4529(14)	3101(28)
C(26)	6451(12)	2857(15)	4938(30)
C(27)	5723(11)	855(15)	5120(29)
C(21)	5251(7)	1040(9)	4319(19)
N(21)	5685(8)	3763(11)	3521(21)
N(22)	6053(8)	2235(11)	4681(22)
N(23)	6214(9)	1422(12)	5251(23)
N(24)	5833(11)	96(14)	5876(29)
C(1)	5461(8)	2802(12)	-219(21)
C(2)	6271(10)	2291(16)	-1294(26)
C(3)	6020(8)	1868(12)	1138(22)
C(4)	4729(7)	2837(10)	5385(21)
C(5)	3856(9)	2571(13)	6345(24)
C(6)	4114(7)	2009(11)	3941(20)
C(7)	2728(10)	1665(18)	8099(35)
C(8)	2344(14)	1149(25)	5675(48)
C(9)	2973(14)	355(25)	7047(50)
N(1)	5913(9)	2328(14)	-177(25)
N(2)	4230(9)	2480(13)	5252(23)
N(3)	2708(13)	1107(23)	6944(46)

[a] All values x 10^4 except those of Eu which are x 10^5. These values are in fractional coordinates.

Table VIII

Final Positional Parameters for Non-hydrogen Atoms in $La(DFBPSC)(NO_3)_3 \cdot 3H_2O$[a]

ATOM	X	Y	Z
LA	78476(7)	66540(5)	72893(4)
C(11)	6377(15)	9614(10)	6293(9)
C(12)	6184(15)	10755(10)	5737(10)
C(13)	6947(16)	11074(10)	4799(11)
C(14)	7848(15)	10263(11)	4460(9)
C(15)	8019(13)	9143(10)	5062(8)
C(16)	5510(17)	9232(10)	7237(10)
C(17)	4964(16)	6726(11)	9145(9)
C(11)	5948(11)	6075(7)	8862(6)
N(11)	7306(11)	8812(8)	5974(8)
N(12)	5648(12)	8180(9)	7764(7)
N(13)	4777(15)	7845(9)	8637(9)
N(14)	4053(20)	6398(11)	9974(10)
C(1)	4978(14)	6495(9)	6507(6)
C(2)	6944(11)	5991(8)	5652(7)
C(3)	4563(13)	6321(10)	5014(9)
C(21)	10548(14)	6593(10)	5194(8)
C(22)	11025(15)	6656(11)	4203(9)
C(23)	10440(17)	7568(13)	3445(9)
C(24)	9447(13)	8376(12)	3739(10)
C(25)	9039(14)	8262(10)	4738(9)
C(26)	11160(14)	5656(10)	5981(9)
C(27)	10690(16)	4796(11)	8575(9)
N(21)	9559(11)	7372(8)	5448(6)
N(22)	10555(12)	5552(9)	6855(9)
N(23)	11198(13)	4724(9)	7629(7)
N(24)	11448(16)	4098(12)	9339(8)
C(21)	9575(11)	5456(8)	8691(6)
N(2)	10115(17)	8191(11)	8163(11)
C(4)	10450(15)	7900(11)	7364(9)
C(5)	8761(14)	7887(10)	8604(9)
C(6)	11101(19)	8761(19)	8527(14)
N(1)	5487(13)	6264(9)	5697(8)
C(7)	5806(18)	6341(12)	2740(20)
C(8)	5338(38)	8300(16)	2108(14)
C(9)	6979(38)	8105(29)	1122(29)
N(3)	6140(40)	7540(27)	1961(25)
C(W1)	7175(12)	4462(7)	7653(7)
C(W2)	11606(19)	7555(12)	10922(10)
C(W3)	6278(25)	10051(22)	10648(18)

[a] All values x 10^4 except those for La which are x 10^5. These values are fractional coordinates.

Table IX

Final Positional Parameters for Non-hydrogen Atoms in $[Hg(DFBPSC)(NO_3)_2]_2$[a]

ATOM	X	Y	Z
HG	4742(7)	12500 *	12500 *
C(11)	847(10)	117(10)	132(16)
C(12)	1035(10)	-274(10)	-534(18)
C(13)	1295(10)	-35(9)	-1293(20)
C(14)	1378(9)	582(10)	-1345(17)
C(15)	1200(11)	921(9)	-606(14)
C(16)	540(10)	-108(10)	917(15)
C(17)	-243(12)	501(12)	2699(18)
C(11)	-195(8)	1054(6)	2510(12)
N(11)	953(8)	698(7)	114(12)
N(12)	323(7)	269(8)	1465(11)
N(13)	18(9)	75(7)	2181(14)
N(14)	-544(10)	320(10)	3421(14)
C(1)	606(10)	-1267(10)	2312(15)
C(2)	45(10)	-1875(9)	2959(15)
C(3)	-275(11)	-1058(9)	2537(21)
N(1)	123(14)	-1361(11)	2594(18)

[a] All values x 10^4 except those of Hg which are x 10^5. These values are fractional coordinates.

* Required by symmetry to be equal to this value.

Table X

Final Temperature Parameters for Non-hydrogen Atoms
$Eu(DFBPSC)(NO_3)_3 \cdot 2H_2O$[a]

ATOM	U11	U22	U33	U12	U13	U23
EU	499(6)	266(4)	261(4)	-17(5)	45(3)	-19(6)
C(11)	69(17)	31(13)	37(12)	5(10)	1(11)	-6(9)
C(12)	101(21)	37(15)	41(13)	15(12)	22(13)	1(11)
C(13)	93(20)	45(15)	25(12)	14(12)	22(11)	1(10)
C(14)	116(22)	19(12)	40(13)	3(12)	27(13)	0(10)
C(15)	62(15)	34(12)	25(10)	-11(10)	13(9)	-9(10)
C(16)	91(19)	48(15)	21(11)	14(12)	11(11)	7(10)
C(17)	63(16)	34(13)	35(12)	7(10)	-7(11)	-8(10)
C(11)	70(11)	25(8)	38(8)	3(6)	-4(7)	-5(6)
N(11)	80(14)	32(11)	23(9)	2(9)	17(9)	0(7)
N(12)	70(12)	38(11)	28(8)	1(9)	-7(7)	-4(8)
N(13)	64(14)	35(11)	52(12)	3(9)	3(9)	-11(9)
N(14)	71(16)	54(14)	92(17)	3(11)	-11(12)	-30(12)
C(21)	90(19)	37(14)	26(12)	-21(12)	16(11)	2(9)
C(22)	100(22)	48(17)	59(17)	-17(14)	19(15)	0(13)
C(23)	115(25)	57(20)	65(19)	-12(16)	22(16)	-16(15)
C(24)	67(18)	39(15)	90(19)	-7(12)	11(14)	3(13)
C(25)	84(18)	33(14)	32(12)	-6(11)	31(11)	-10(10)
C(26)	106(20)	33(15)	44(13)	-20(12)	22(12)	-6(12)
C(27)	62(17)	48(15)	35(13)	-2(11)	5(11)	7(10)
C(21)	54(10)	45(9)	38(8)	-4(7)	-8(7)	6(6)
N(21)	60(13)	27(10)	32(10)	-4(8)	8(8)	-1(7)
N(22)	64(12)	27(10)	37(9)	-4(8)	2(8)	-6(8)
N(23)	71(14)	40(12)	35(10)	-3(9)	-5(9)	6(8)
N(24)	91(17)	51(14)	62(15)	-3(11)	-3(12)	18(11)
C(1)	93(13)	65(12)	42(9)	-2(9)	17(8)	11(8)
C(2)	137(19)	116(18)	56(12)	7(14)	56(11)	-6(12)
C(3)	68(12)	76(13)	52(10)	0(9)	18(8)	-7(9)
C(4)	81(12)	40(10)	54(10)	-1(8)	18(8)	-14(7)
C(5)	118(15)	81(15)	58(11)	-7(11)	37(9)	-15(10)
C(6)	52(11)	67(11)	49(9)	2(7)	9(7)	-13(8)
C(7)	84(17)	143(22)	120(20)	-20(14)	-6(14)	-24(16)
C(8)	121(23)	237(37)	144(26)	-22(22)	-24(19)	-3(25)
C(9)	136(27)	183(33)	207(33)	13(22)	-10(23)	-31(26)
N(1)	88(15)	56(14)	44(11)	-10(11)	24(9)	8(11)
N(2)	74(13)	61(15)	34(10)	6(10)	24(8)	3(9)
N(3)	85(22)	152(29)	133(27)	-16(18)	-31(18)	12(21)

[a] All values x 10^4 except those for Eu which are x 10^5.

Table XI

Final Temperature Parameters for Non-hydrogen Atoms in $La(DFBPSC)(NO_3)_3 \cdot 3H_2O$[a]

ATOM	U11	U22	U33	U12	U13	U23
LA	248(5)	215(5)	242(5)	56(2)	42(2)	-19(3)
C(11)	37(6)	23(6)	27(6)	6(5)	2(5)	-1(5)
C(12)	36(7)	19(6)	49(8)	3(5)	-2(6)	3(5)
C(13)	39(7)	19(6)	53(9)	2(5)	-9(6)	5(6)
C(14)	35(7)	38(7)	22(6)	-3(5)	-1(5)	6(5)
C(15)	23(6)	27(6)	28(6)	-1(4)	0(5)	-2(5)
C(16)	48(8)	22(6)	48(8)	15(5)	4(6)	-8(6)
C(17)	45(7)	31(7)	26(6)	9(6)	10(5)	-5(5)
C(11)	47(5)	29(4)	33(5)	13(4)	11(4)	-1(4)
N(11)	24(5)	20(5)	46(6)	2(4)	2(4)	0(4)
N(12)	36(5)	33(6)	21(5)	11(4)	-2(4)	-8(4)
N(13)	60(7)	26(6)	43(7)	14(5)	27(5)	-3(5)
N(14)	107(11)	33(7)	57(8)	21(7)	58(8)	6(6)
C(1)	43(5)	72(6)	8(4)	12(4)	-8(3)	-17(4)
C(2)	28(5)	49(5)	49(6)	0(4)	7(4)	-13(4)
C(3)	45(6)	57(6)	69(7)	9(5)	-15(5)	-14(5)
C(21)	26(6)	33(6)	22(6)	-1(5)	-2(4)	-5(5)
C(22)	33(6)	45(7)	22(6)	0(5)	2(5)	-13(5)
C(23)	53(8)	52(8)	19(6)	4(6)	10(5)	-6(6)
C(24)	52(8)	40(8)	34(8)	6(6)	3(6)	7(6)
C(25)	24(6)	32(6)	26(6)	-1(5)	4(4)	-3(5)
C(26)	24(6)	32(6)	34(7)	4(5)	14(5)	-13(5)
C(27)	45(7)	33(7)	28(7)	11(6)	0(5)	-5(5)
N(21)	27(5)	22(5)	17(5)	0(4)	-1(3)	-3(4)
N(22)	24(5)	27(5)	57(8)	15(4)	-1(5)	-11(5)
N(23)	43(6)	37(6)	23(5)	20(5)	6(4)	0(4)
N(24)	71(8)	66(8)	26(6)	39(7)	-15(5)	-11(5)
C(21)	41(5)	38(5)	30(5)	17(4)	1(3)	-5(3)
N(2)	61(9)	48(7)	64(9)	-4(6)	-6(7)	-16(6)
C(4)	83(8)	65(7)	56(7)	-37(6)	24(6)	-12(6)
C(5)	55(7)	59(7)	68(7)	4(5)	10(5)	-25(5)
C(6)	79(9)	197(19)	132(13)	-33(11)	0(9)	-126(14)
N(1)	30(6)	24(5)	45(7)	-3(4)	-19(5)	2(4)
C(7)	47(8)	53(7)	379(26)	14(6)	-15(11)	-68(11)
C(8)	513(36)	147(12)	174(21)	223(18)	-20(21)	-55(13)
C(9)	239(26)	220(30)	329(37)	-92(22)	134(26)	-19(26)
N(3)	298(27)	133(24)	195(27)	137(23)	-118(22)	-80(21)
C(W1)	49(5)	25(4)	55(6)	1(4)	8(4)	-4(4)
C(W2)	105(11)	65(8)	77(8)	28(7)	21(7)	-5(6)
C(W3)	109(15)	206(19)	186(19)	15(14)	-3(13)	-144(17)

[a] All values x 10^4 except those for La which are x 10^5.

Table XII

Final Temperature Parameters for Non-hydrogen Atoms in $[Hg(DFBPSC)(NO_3)_2]_2$[a]

ATOM	U11	U22	U33	U12	U13	U23
HG	4384(101)	1722(77)	3891(87)	0 *	0 *	-107(96)
C(11)	20(16)	36(17)	38(17)	2(13)	2(12)	15(13)
C(12)	21(16)	27(14)	69(20)	9(11)	-17(13)	-16(14)
C(13)	36(15)	25(13)	59(16)	3(11)	-31(26)	-13(13)
C(14)	23(16)	67(18)	39(16)	-5(12)	-20(13)	-28(15)
C(15)	9(14)	46(13)	25(13)	-3(14)	-4(13)	4(11)
C(16)	27(16)	21(13)	37(16)	8(12)	-7(12)	-6(11)
C(17)	47(19)	47(18)	30(16)	-4(15)	-14(14)	8(14)
C(11)	64(14)	19(11)	44(12)	-6(8)	16(10)	-1(9)
N(11)	28(12)	19(11)	34(13)	7(9)	-2(10)	2(9)
N(12)	25(14)	23(11)	24(15)	1(9)	0(9)	21(9)
N(13)	48(15)	15(10)	41(15)	3(11)	-7(11)	-2(10)
N(14)	62(19)	55(15)	41(16)	-11(13)	10(13)	3(10)
O(1)	79(19)	61(14)	96(17)	-8(15)	-25(14)	-3(15)
O(2)	94(20)	73(16)	134(19)	10(14)	17(16)	31(14)
O(3)	81(23)	76(14)	181(32)	-13(13)	-42(21)	10(16)
N(1)	66(25)	105(20)	97(20)	-6(17)	-5(18)	-7(14)

[a]All values x 10^4 except for Hg which are x 10^5.

*Required by symmetry to be equal to zero.

complexes amounts to the expected difference of 0.15 Å in their crystal radii for the two different coordination numbers as compiled by Shannon.[43]

Inspection of the metal-to-donor bond lengths in these two DFBPSC complexes shows that the Ln-O bonds to be substantially shorter than the Ln-N bonds. The average La-O bond length is 2.63 Å while the average La-N bond length is 2.76 Å. A similar difference is observed in the Eu(III) case. The average Eu-O bond length is 2.48 Å while the average Eu-N bond length is 2.61 Å. Although the lanthanides have been characterized as hard acids[46] and accordingly would be expected to interact more strongly with the harder bases, the oxygen donors, in these instances steric effects and the geometrical constraints of the ligand cannot be overlooked. The lanthanide ion will reside in the cavity formed by the ligand in a place where it can maximize the bonding with the ligand and any other potential donors while keeping steric effects to a minimum. By residing closer to the carbonyl oxygen and therefore further from the bipyridyl group, steric interactions between the bidentate nitrate ions [and the water molecule in the La(III) case] and the ligand will be minimized. There has not been a great deal of structural data accumulated on the lanthanides with mixed donor complexes to make any statements concerning the preferential coordination to oxygen or nitrogen donors. Variations will occur due to differences in the size of donor atoms, state of hybridization, substituent effects on the ligands, and steric effects between these ligands.

The dihedral angle between the two substituted pyridine rings in the La compound is 20.9°. This is a substantial twist. For the Eu compound this angle is closer to the more commonly observed values and amounts to 10.5°. A dihedral angle of 12.6° has been reported for La(2,2'-bipyridine)$_2$-$(NO_3)_3$,[61] a ten coordinate compound. Table XIII lists the dihedral angles and least-squares planes for the three complexes.

The pyridine rings for the three complexes are essentially planar with the largest deviation from planarity being 0.04 Å for atom C(13) in the Eu complex. The sidearms are rotated out of the plane of the pyridine ring to which they are bound in all complexes. Such flexibility has been observed for DAPSC[10,26,74] and analogous compounds[8,75] studied in this lab. The extent of this rotation is slightly different for the two halves of the ligand in both Ln(III) compounds. The dihedral angle between the pyridine ring I in the La(III) compound defined by atoms N(11), C(11) to C(15) and sidearm I defined by atoms O(11), N(12) to N(14), C(16) and C(17) amounts to 8.2°. For pyridine ring II defined by atoms N(21), C(21) to C(25) and sidearm II defined by atoms O(21), N(22) to N(24), C(26) and C(27), the angle is slightly greater and amounts to 11.8°. For the Eu(III) compound these dihedral angles are 9.8° and 13.5°, respectively. It is interesting to note that the direction of the twist is different for the two compounds. For the Eu(III) compound the dihedral angle between the

least-squares planes of the two sidearms is 32.8°. This is approximately equal to the sum of the dihedral angles between the sidearms and the pyridine rings and between the pyridine rings themselves. This means the sidearms twist in the opposite directions. This has the effect of increasing the cavity size of the ligand over what it would be if the two halves of the ligand remained planar. In the La(III) compound the dihedral angle between the two sidearms is 31.7°. This is substantially less than the sum of the various dihedral angles and indicates that the two sidearms twist in the same direction. This can also be seen by the fact that atoms O(21) and N(22) lie on the same side of the least-squares plane through pyridine ring II as does sidearm I. Presumably such a difference is brought about by the substantially larger dihedral angle between the pyridine rings in the La(III) compound. Table XIV lists the distances between donor atoms in the ligand for the two compounds. The distances in the eleven coordinate La(III) compound are on the average 0.17 Å greater than those found for the ten coordinate Eu(III) compound which is consistent with the size differential for these two ions given their coordination number.

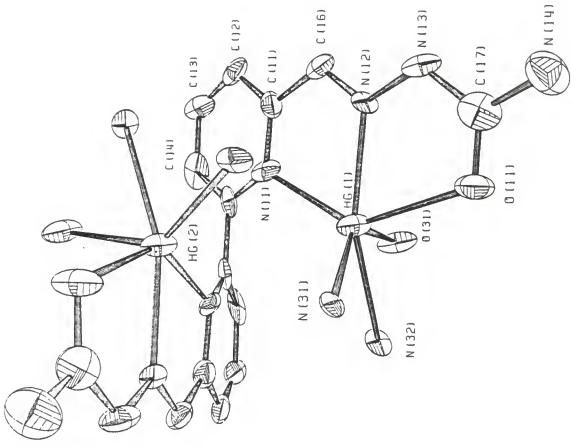
The difference in coordination number for the two lanthanide ions is most likely the result of differences in ion sizes due to the lanthanide contraction. The larger La(III) ion can accommodate an additional donor without the interligand repulsive energies becoming prohibitive. Such changes

in coordination number with changing ion size have also been observed in other Ln(III) complexes as well.[76-80] Close, nonbonded contacts for the donor atoms of the Eu(III) compound and the La(III) compound are found in Table XV and Table XVI, respectively.

In sharp contrast to the results with the La(III) and the Eu(III) compounds, the Hg(II) compound was found to be a six coordinate dimeric species with the two halves of the ligand coordinated to different Hg(II) ions. An ORTEP[71] drawing of one full ligand, the two mercury ions, and the coordination sphere from the second ligand is shown in Figure 6. The two Hg(II) ions are separated by more than 3.6 Å. This is greater than twice the van der Waals radii for Hg[81] and as a result there can be no significant interaction between the two ions. The dihedral angle between the two pyridine rings is 52.9°. This amounts to the largest reported dihedral angle for such a ligand to date with the exception of compounds with substituents in the 3 and 3' positions[82] or N, N' substituted compounds.[83] The extent of this twist in the compound is the result of two factors both of which are steric in nature. The angle has to be great enough to allow coordination to the two Hg(II) ions while minimizing the steric effects between these two large ions. The second factor has to do with steric effects between the two ligands themselves. In order to coordinate in a dimeric fashion a substantial twist between the two halves of the ligand is necessitated to prevent prohibitive steric

Figure 6

ORTEP Drawing and Atomic Numbering Scheme for $[Hg(DFBPSC)(NO_3)_2]_2$


C(14)
C(13)
C(12)
C(11)
C(16)
N(13)
C(17)
N(14)
N(11)
HG(1)
N(12)
O(31)
O(11)
HG(2)
N(31)
N(32)

interactions between the two ligands. In this present structure the closest approach of any atom in one ligand to another atom in the second ligand is 3.31 Å. This is between N(12) and atom N(41) which is related by symmetry to atom N(11).

Six coordination is not very common in Hg chemistry,[52,81,84] although a few such compounds have been structurally characterized.[85-91] These compounds can be placed into two general categories: compounds in which the Hg-to-donor distances are equivalent[85-90] and those compounds whose coordination can be described as 2 + 4 complexes.[91] These latter complexes derive their name from the fact that there exists in these species two approximately colinear donor atoms whose bond lengths to Hg(II) are shorter by 0.5 Å or more than the bond lengths of the other four donors. The 2 + 4 complexes frequently occur in cases where the Hg(II) is part of the infinite, three-dimensional lattice. Monomeric complexes are found in the instances where the coordination is symmetric.[85-90]

In the $(Hg(DFBPSC)(NO_3)_2)_2$ compound, the bonding more closely resembles that of the symmetrically bonded compounds, although the donor-to-Hg bond lengths are not equivalent. The shortest bond length is 2.268(18) Å for the Hg-to-N(12) bond. The longest distance is 2.485(18) Å for the O(11)-to-Hg bond, while N(11) has a bond length to Hg of 2.385(18) Å. This is in contrast to the results found with the Ln(III) ions. In the lanthanide complexes steric effects and

coordination by other ligands determined the relative position of the ion in the cavity formed by the ligand. In this present instance there are no other coordinating groups. The Hg(II) will coordinate most strongly with the best donors in the ligand which are the nitrogen donors with the result that the coordination is asymmetric. It is important to point out that the atoms that have the shortest bonds to Hg, atoms N(12) and the symmetry equivalent N(32), are nearly colinear. The bond angle between atoms N(12), Hg and N(32) is 164°. Instances where the two strongest interactions with Hg occur between atoms that are nearly colinear with Hg have been observed in structures where the bonding might have been thought to be more symmetric. Coordination of 2,2'-bipyridine with methylmercury results in an asymmetric coordination of bipyridine with one Hg-to-N bond nearly 0.2 Å shorter than the other.[92] This atom forms an angle of 172° with the methylmercury group. Slightly longer differences in bond length are observed for 4,4',4"-triethylterpyridine methylmercury complex with the N atom with the shortest bond to Hg forming an angle of 170° with the Hg atom and methyl group.[93]

The mode of coordination by the ligand resulted in an interesting and unexpected six coordinate, dimeric complex. There are a variety of coordination geometries that are possible in this situation. The resulting complex could have resembled that found for the Ln(III) ions resulting in a ten or an eleven coordinate species. Eight coordination

was expected with two donors in the apical position relative to the ligand. A third possibility would be a complex that resembled the geometry found for the seven coordinate $Co(DABPSC)(NO_3)_2$.[41] Thus one carbonyl donor would be rotated out of bonding position. The ligand would then coordinate through only five of the donors. That such a complex is possible for Hg(II) is evident from the results with DAPSC.[9] The Hg(II) fits into the cavity formed by DAPSC which would be approximately the same size as that for DFBPSC or DABPSC coordinating in a pentadentate fashion as described above. That none of the above compounds result is indicative of the coordination chemistry of Hg(II) and the flexibility of the ligand. The coordination chemistry of Hg(II) is characterized by compounds of low coordination number.[52,81,84] A dimeric species allows for a minimum coordination number while allowing full coordination by the ligand. In view of other Hg(II) compounds structurally characterized, the ligand is expected to provide the best donors. These results show that water molecules and nitrate ions do not compete very well with donors such as pyridine or bipyridine for coordination sites on Hg.[92,94-98]

The difference in the mode of coordination between the Ln(III) ions and the Hg(II) ion is most likely the result of the difference in the bonding in the various complexes. For the Ln(III) ions the bonding is essentially ionic. In such complexes the coordination number is a function of the size of the ions and the molecules in the complex.[99] The

use of chelating groups such as DFBPSC and nitrate ion minimize the steric crowding around the cation and allow for uncommonly high coordination numbers. In the case of Hg(II) the bonds have more covalent character which is reflected in the lower coordination number. The lower coordination number allows for shorter and therefore stronger bonds. The unusual dimeric fashion in which the ligand coordinates can be interpreted as a means of minimizing the number of donors to Hg(II) so that shorter, stronger covalent bonding can occur.

The bond distances in the bipyridyl part of the ligand are comparable to those found in the uncoordinated molecule.[53] The bond angles in each ring are similar to those found in the molecule as well. Upon coordination of the two nitrogen atoms to a metal ion, distortions of the ligand occur. The bond angle between atoms N(11), C(15) and C(25) and N(21), C(25) and C(15) are less than 120° in all three compounds. The observed angles for the La(III) compound are 116.5(10)° and 117.3(10)°, respectively, and for the Eu(III) compound they are 114.4(14)° and 117.8(14)°, respectively. For the Hg(II) compound the observed angle for atoms N(11), C(15) and C(25) is 116,4(19)°. The angle between atoms N(21), C(25) and C(15) is required by symmetry to be equal to this value. Such distortions are found in other bipyridyl complexes as well. The observed bond distances and angles in the semicarbazone sidearms are similar to those found in the DAPSC complexes.

In a review on coordination by nitrate ions, Addison et al.[100] describe in detail a wide variety of bonding modes that have been observed for metal nitrate compounds. In light of the large body of data accumulated on nitrate coordination to the lanthanides, it is clear that the normal mode of binding is in a symmetric, bidentate fashion.[101-112] This type of coordination is observed for the two Ln(III) ions. In both cases two of the three nitrates are coordinated in such a fashion while the third is uncoordinated. Presumably this is due to the already sterically hindered coordination around the lanthanides. Table XVII lists the bond distances and angles for the nitrate ions for the three compounds. It can be seen from this table that the bond distances and angles for the uncoordinated nitrate ion in the La(III) compound composed of atoms N(3), O(7), O(8) and O(9) deviate drastically from the expected values of 1.26 Å for the bond distance with bond angles of 120°.[100] Associated with these values are rather high esd's. The thermal parameters for all the atoms in this group are also high. Such observations are a sign of disordering in the atomic positions. There has been one report of a disordered, coordinated nitrate,[61] but such examples are uncommon. All the other nitrate ions show values for bond distances and angles that are reasonable for such a group. The nitrate ion in the Hg(II) complex is uncoordinated. In general, nitrate ions do not coordinate to Hg.[113-118] However, atom O(3) appears to be in a position to hydrogen-bond to the

hydrogen atom bound to atom N(13). The hydrogen atom was not located in the difference Fourier map and its position is uncertain. The distance between atoms O(3) and N(13) which is 2.661(28) Å, suggests a strong hydrogen-bond interaction.[119]

Table XIII

Least-Squares Planes and Selected Dihedral Angles for Metal Complexes of DFBPSC

LEAST-SQUARES PLANES

Plane 1			Pyridine Ring I				Metal
Defined by Atoms	N(11)	C(11)	C(12)	C(13)	C(14)	C(15)	
Deviation (Å)	0.010	-0.012	0.003	0.009	-0.010	0.001	La
	0.019	-0.008	-0.025	0.044	-0.032	0.001	Eu
	0.022	-0.036	0.021	0.006	-0.019	0.007	Hg

Plane 2			Pyridine Ring II				Metal
Defined by Atoms	N(21)	C(21)	C(22)	C(23)	C(24)	C(25)	
Deviation (Å)	-0.012	0.004	0.007	-0.010	0.003	0.009	La
	-0.017	0.033	-0.021	-0.005	0.022	-0.011	Eu

Plane 3			Sidearm I				Metal
Defined by Atoms	C(16)	N(12)	N(13)	C(17)	O(11)	N(14)	
Deviation (Å)	-0.002	-0.018	0.028	-0.003	0.008	-0.014	La
	-0.038	-0.004	0.074	0.018	-0.002	-0.048	Eu
	-0.037	0.038	0.023	-0.006	-0.010	-0.009	Hg

Plane 4			Sidearm II				Metal
Defined by Atoms	C(26)	N(22)	N(23)	C(27)	O(21)	N(24)	
Deviation (Å)	0.084	-0.027	-0.127	-0.005	0.006	0.068	La
	0.067	-0.001	-0.131	0.001	-0.006	0.070	Eu

DIHEDRAL ANGLES (°)

	La	Eu	Hg
Plane 1 - Plane 2	20.9	10.5	52.9
Plane 1 - Plane 3	8.2	9.8	12.1
Plane 2 - Plane 4	11.8	13.5	*
Plane 3 - Plane 4	31.7	32.8	73.1

*Required by symmetry to be equal to the value for Plane 1 - Plane 3.

Table XIV

Interatomic Distances between Donor Atoms in Lanthanide Complexes of DFBPSC

	Eu	La
N(11)-N(21)	2.710(19)	2.718(14)
N(11)-N(12)	2.623(18)	2.725(13)
N(11)-O(11)	4.405(16)	4.585(13)
N(11)-N(22)	4.571(18)	4.619(15)
N(11)-O(21)	4.956(16)	5.134(13)
N(12)-O(11)	2.589(17)	2.590(13)
N(12)-N(21)	4.538(19)	4.730(13)
N(12)-N(22)	5.190(19)	5.396(14)
N(12)-O(21)	4.300(17)	4.542(13)
O(11)-N(21)	4.951(16)	5.388(12)
O(11)-N(22)	4.291(17)	4.763(13)
O(11)-O(21)	2.807(15)	3.091(12)
N(21)-N(22)	2.617(17)	2.664(14)
N(21)-O(21)	4.353(16)	4.490(12)
N(22)-O(21)	2.570(17)	2.611(13)

Table XV

Close Non-bonded Contacts for Donor Atoms in $Eu(DFBPSC)(NO_3)_3 \cdot 2H_2O$ (<3.0 Å)

N(11)-N(21)	2.710(19)
N(11)-N(12)	2.623(18)
N(12)-O(11)	2.589(17)
N(12)-O(6)	2.758(17)
O(11)-O(21)	2.807(15)
O(11)-O(3)	2.893(17)
N(21)-N(22)	2.617(17)
N(22)-O(21)	2.570(17)
N(22)-O(3)	2.780(17)
O(21)-O(6)	2.907(16)
O(1)-O(3)	2.177(18)
O(4)-O(6)	2.125(17)

Table XVI

Close Non-bonded Contacts for Donor Atoms in $La(DFBPSC)(NO_3)_3 \cdot 3H_2O$ (<3.0 A)

N(11)-N(21)	2.717(13)
N(11)-N(12)	2.724(14)
N(12)-O(11)	2.593(14)
N(12)-O(5)	2.827(15)
O(11)-O(w1)	2.982(13)
N(21)-O(2)	2.669(13)
N(21)-O(4)	2.968(15)
N(21)-N(22)	2.666(14)
N(22)-O(21)	2.611(14)
O(21)-O(5)	2.924(15)
O(21)-O(w1)	2.884(13)
O(w1)-O(2)	2.916(14)
O(1)-O(2)	2.145(13)
O(4)-O(5)	2.171(17)

Table XVII

Interatomic Distances and Angles for Nitrate Groups

	Eu	La	Hg
Distances:			
N(1)-O(1)	1.267(22)*	1.272(14)*	1.258(40)
N(1)-O(2)	1.220(23)	1.246(14)*	1.256(33)
N(1)-O(3)	1.267(20)*	1.216(16)	1.194(38)
N(2)-O(4)	1.231(20)*	1.256(19)*	
N(2)-O(5)	1.217(21)	1.264(18)*	
N(2)-O(6)	1.268(18)*	1.246(24)	
N(3)-O(7)	1.281(32)	1.574(39)	
N(3)-O(8)	1.213(36)	1.168(41)	
N(3)-O(9)	1.329(42)	1.357(50)	
Angles:			
O(1)-N(1)-O(2)	122.1(16)	116.8(10)	118.5(26)
O(1)-N(1)-O(3)	118.4(15)	119.9(11)	121.0(28)
O(2)-N(1)-O(3)	119.5(16)	123.2(11)	120.6(28)
O(4)-N(2)-O(5)	121.1(15)	119.0(14)	
O(4)-N(2)-O(6)	116.5(14)	121.0(15)	
O(5)-N(2)-O(6)	122.4(15)	120.0(15)	
O(7)-N(3)-O(8)	121.8(25)	113.4(27)	
O(7)-N(3)-O(9)	121.0(24)	146.2(30)	
O(8)-N(3)-O(9)	116.4(27)	100.8(30)	

*Indicates oxygen atom is coordinated to metal.

CHAPTER THREE

POLYHEDRAL ANALYSIS OF LANTHANIDES

X-ray crystallographic techniques are the best methods for deriving detailed structural information about high coordination complexes. As the number of structurally characterized high coordination complexes increases, it becomes useful to be able to systematize their geometries in terms of some idealized polyhedra.

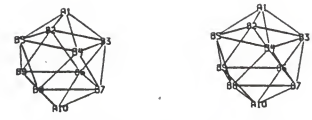
It would be quite tedious and not very useful to discuss a compound in terms of the large number of ideal polyhedra that are possible for a given coordination number.[120] Hoard and Silverton[121] have enumerated the contributions to the energy of any such polyhedra. The contributions that seem most generally applicable to a discussion of high coordination complexes are the direct interaction of the central atom with the donor atoms and the interligand repulsions. If the metal-to-donor distance is assumed constant then the controlling factor in determining the coordination geometry will be the minimization of the interligand repulsions. This minimization of repulsive energies forms the starting point for discussion of coordination geometries in terms of ideal polyhedra in a number of studies.[1,2,122]

The total repulsive energy for a particular polyhedron is assumed to be given by the equation of the form:

$$E = \sum_{i \neq j} r_{ij}^{-n},$$

where n is an integer and r is the distance between ligands i and j. Most high coordination complexes contain chelating ligands, and the geometrical contraints of these ligands will often influence the geometry a complex will assume. Such complexes will frequently deviate from the ideal polyhedra. The present discussion will compare the geometries of the Eu and La compounds with those of some ideal polyhedra and will make an estimate of the deviation from ideality in each case.

The Eu and La compounds discussed so far have been shown to be ten and eleven coordinate, respectively. Neither ten nor eleven coordination can be considered at all common. However, there are more examples of the former.[1] A recent survey of the literature revealed only seven reported examples of eleven coordination for the rare earth elements.[123] For ten coordination, two important polyhedra will be considered. These are the bicapped square antiprism (BCSAP) and the decatetrahedron (DTH). Both are shown in Figure 7. For eleven coordination, the monocapped pentagonal antiprism (MCPAP) and the decahexahedron (DHH) will be used as the model geometries. The MCPAP is shown in Figure 8, and the DHH is shown in Figure 9. It can be seen in Figure 8 that the MCPAP can be derived from the icosahedron by the removal of one vertex. These model geometries conform to polyhedra of minimum repulsive energy using the equation given above.

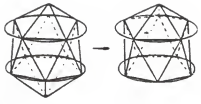


Bicapped-Square Antiprism

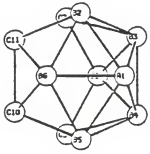
Decatetrahedron

Figure 7

Stereoscopic Drawing for Bicapped-Square Antiprism and Decatetrahedron



Monocapped-Pentagonal Antiprism — Icosahedron



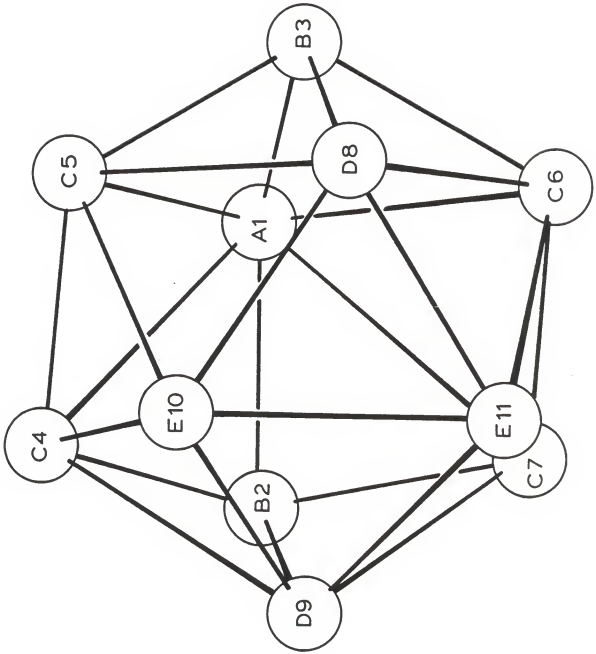
Monocapped-Pentagonal Antiprism

Figure 8

Illustration of Monocapped-Pentagonal Antiprism and Icosahedron

Figure 9

Illustration of Decahexahedron


B3
C5
D8
C6
A1
C4
E10
E11
C7
B2
D9

In addition to these polyhedra and in view of the hexadentate nature of the ligand DFBPSC, the observed coordinates of the Eu and La compounds will be compared to a model that utilizes six vertices in a plane. For the Eu compound a 2-6-2 model will be used with six vertices in the xy plane, two vertices in the xz plane with z positive , and two in the yz plane with z negative. For the La compound a 2-6-3 model will be used. All distances to the origin will be normalized for all model polyhedra.

The first step in comparing an observed coordination sphere with that of a model polyhedron is the assignment of donor atoms in the observed complex to vertices in the model. To do this the number of faces meeting at each vertex in the coordination sphere of the model and the metal complex is calculated. Comparison of these results allows assignments to be made. Once an atom-to-vertex correspondence is made, a quantitative estimate of the degree of distortion from ideality can be obtained. Two different methods are used to do this. The first method is based on a suggestion by Porai-Koshits and Aslanov.[124] Dihedral angles, called δ angles, between normals to faces that meet at each edge in the polyhedron are calculated for both the model and the observed coordination sphere. However, Robertson's[2] suggestion of reducing the observed coordination to points on a unit sphere to remove effects of unequal bond lengths on the δ angles will not be followed here. The δ angles of the observed coordination sphere are compared to those for the

model. The minimum root-mean-square value is assumed to be found for the model that best describes the geometry of the observed coordination sphere. The atom-to-vertex correspondence for the Eu(III) compound and the La(III) compound for the proposed model geometries is shown in Table XVIII and Table XIX, respectively. A list of the δ angle values is shown in Table XX for the Eu(III) compound and in Table XXI for the La(III) compound.

A second method for determining the degree of distortion is that suggested by Dollase[125] in which the atomic coordinates of the donor atoms are compared to the vertices of the model polyhedron. First, the coordinates of the vertices of the model are placed on the same scale and origin as the atomic coordinates by using the average donor-to-metal distance as the distance of each vertex to the origin. The coordinates of the donor atoms are held fixed while those of the model are rotated to minimize the average distance between corresponding atoms of the two sets. The polyhedron that has the minimum value for the root-mean-square of the difference between the coordinates of the model and the observed atomic coordinates is assumed to provide the best description of the geometry of the complex. The results of such calculations are shown on Table XXII for the Eu(III) compound and Table XXIII for the La(III) compound.

Analysis of the geometries of ten coordinate compounds revealed that most have coordination spheres that can be

Table XVIII

Atom-to-Vertex Correspondence for $Eu(DFBPSC)(NO_3)_3 \cdot 2H_2O$

BCSAP		DTH		2-6-2	
A1	N(22)	A1	O(6)	A1	O(21)
B2	N(21)	A2	O(4)	A2	O(11)
B3	O(3)	B3	O(21)	A3	N(12)
B4	O(21)	B4	N(11)	A4	N(11)
B5	O(4)	C5	N(22)	A5	N(21)
B6	N(11)	C6	N(21)	A6	N(22)
B7	O(6)	C7	N(12)	B7	O(3)
B8	O(11)	C8	O(11)	B8	O(1)
B9	O(1)	D9	O(1)	C9	O(6)
A10	N(12)	D10	O(3)	C10	O(4)

Table XIX

Atom-to-Vertex Correspondence for $La(DFBPSC)(NO_3)_3 \cdot 3H_2O$

MCPAP		DHH		2-6-3	
A1	O(1)	A1	N(11)	A1	O(21)
B2	N(11)	B2	N(12)	A2	N(22)
B3	N(12)	B3	N(21)	A3	N(21)
B4	O(11)	C4	O(1)	A4	N(11)
B5	O(w1)	C5	O(2)	A5	N(12)
B6	O(2)	C6	O(4)	A6	O(11)
C7	O(4)	C7	O(5)	B7	O(4)
C8	O(5)	D8	N(22)	B8	O(5)
C9	O(21)	D9	O(11)	C9	O(w1)
C10	N(22)	E10	O(w1	C10	O(1)
C11	N(21)	E11	O(21)	C11	O(2)

best described as a DTH,[1,2] although a few have been found to more closely resemble a BCSAP.[2,11,126,127] In a review on high coordination complexes, Drew refers to the DTH as a 4A-6B expanded dodecahedron. The designation of this shape as a DTH was suggested by Robertson[2] and is used here. Due to the lack of structural data, no detailed analysis of the geometry of eleven coordination has been undertaken.

The results using either of the two methods described show that the best fit is obtained for the Eu(III) compound with a BCSAP and for the La(III) compound with a DHH. The geometries of the previously reported ten[10] and eleven[11] coordinate lanthanide complexes studied in this lab were also best described as a BCSAP and a DHH, respectively.

One requirement for an observed coordination sphere to fit the BCSAP model is the existence of a donor-metal-donor bond angle close to 180°. These two donors would then satisfy, in part, the requirements of the capping vertices. This requirement is met by two donors in the ligand DFBPSC. The atoms N(12) and N(22) form an angle of 178° with the Eu atom. The number of faces meeting at each apex is four and this requirement is also met by these two atoms. The assignment of the atoms N(12) and N(22) to the capping vertices A10 and A1 was made on this basis. The rest of the assignments can be made quite readily due to the nature of the least-squares plane of the ligand and one below at approximately right angles to each other. The dihedral angle between the plane defined by the vertices A10, B6 and B8

which correspond to the atoms N(12), N(11) and O(11), respectively, and the plane defined by the vertices A1, B2 and B4 which correspond to the atoms N(22), N(21) and O(21), respectively, is exactly 45° in the model but only 25.5° in the actual structure. Deviations will also arise from the difference in bond lengths for the various donor atoms which range from 2.442(10) Å to 2.638(14) Å for the Eu compound. In the ideal polyhedra all the distances from the vertices to the origin are equal. Further deviations will arise from the restriction in edge length, or bite, of the chelating donors. For the nitrate groups for the two compounds, the bite averages 2.15 Å while for DFBPSC the average distance between donors is 2.64 Å. The fit is not perfect by any means for the reasons described above, but the geometry of the Eu compound can be better described as a BCSAP than as a DTH.

In cases where no angle of 180° exists in the model as occurs in the ten coordinate DTH and the eleven coordinate DHH and MCPAP assignment of donor atoms to vertices is more difficult. In these instances the number of faces meeting at each vertex and the knowledge of the geometry of the ligand are useful. In the La(III) compound, assignment of the atom N(11) to vertex A1 in the DHH was made on the basis of the fact that both had six faces meeting at their respective positions. Due to the hexadentate nature of DFBPSC, once an initial assignment is made further assignments are straightforward. It is not surprising that the

geometry of the La compound fit the DHH model better than it did the MCPAP model as it is difficult to fit the hexadentate ligand into the MCPAP model without imparting severe distortions on the geometry.

There have been only a few studies of this kind undertaken on such high coordination compounds. This is due, in part, to the relatively few complexes that have been structurally characterized. It can be argued that any agreement between the geometry of a complex containing chelating ligands whose donor atoms are constrained in some fashion and some ideal polyhedron is fortuitous, insofar as the model assumes that all donors are equivalent and can occupy positions of minimum repulsive energy without constraint. However, the concept of energy minimization is a valid one. This is especially true in the case of the lanthanide and actinide coordination complexes where an ionic model provides a good description of the bonding. Such electrostatic ineteractions are more dependent on bond distances than on the directionality of the bonding. Within the constraints imposed by the nature of the ligands the donors will assume positions that minimize the repulsive interactions with the other donors or groups of donors while maximizing the electrostatic interactions with the metal. In such cases the coordination geometry is an important and interesting part of the structural chemistry of the complex.

Table XX

Delta (δ) Angles between Normals to Planes for $Eu(DFBPSC)(NO_3)_3 \cdot 2H_2O$

Edge	Observed Angle	DTH	Δ	BCSAP	Δ	2-6-2	Δ
N(12)-N(11)	65.88	54.63	11.25	56.34	9.54	64.73	1.15
N(12)-N(6)	59.93	43.28	16.65	56.34	3.59	51.58	8.35
N(12)-O(11)	65.02	65.84	0.82	56.34	8.68	69.77	4.75
N(12)-O(1)	42.14	68.90	26.76	56.34	14.20	49.44	7.30
N(22)-O(4)	40.77	43.28	2.51	56.34	15.57	51.58	10.81
N(22)-O(21)	66.25	54.63	11.62	56.34	9.91	64.73	1.52
N(22)-O(3)	62.07	68.90	6.83	56.34	5.73	49.44	12.63
N(22)-N(21)	67.51	65.84	1.67	56.31	11.20	69.77	2.26
N(11)-O(6)	21.22	45.82	24.60	30.85	9.63	25.13	3.91
N(11)-O(1)	44.94	27.00	17.94	30.85	14.09	51.93	6.99
N(11)-O(4)	39.56	45.82	6.26	56.16	16.60	25.13	14.43
N(11)-N(21)	65.68	54.63	11.05	56.16	9.52	64.73	0.95
O(6)-O(11)	27.79	43.28	15.49	30.85	3.06	51.58	23.79
O(6)-O(4)	69.39	48.21	21.18	56.16	13.23	84.37	14.98
O(6)-O(21)	50.94	45.82	5.12	56.16	5.22	25.13	25.81

O(11)-O(1)	27.07	0	27.07	30.85	3.78	49.44	22.37
O(11)-O(21)	59.93	54.63	5.30	56.16	3.77	64.73	4.80
O(11)-O(3)	52.74	68.90	16.16	56.16	3.42	49.44	3.30
O(1)-O(3)	71.12	78.05	6.93	56.16	14.96	92.60	21.48
O(1)-N(21)	39.87	68.90	29.03	56.16	16.29	49.44	9.57
O(4)-O(21)	28.17	45.82	17.65	30.86	2.69	25.13	3.04
O(4)-N(21)	45.44	43.28	2.16	30.86	14.58	51.58	6.14
O(21)-O(3)	26.38	27.00	0.62	30.86	4.48	51.93	25.55
O(3)-N(21)	19.96	0.00	19.96	30.86	10.90	49.44	29.48
RMS(del) = $\left(\frac{\Sigma\Delta^2}{n}\right)^{\frac{1}{2}}$			15.47		10.48		14.17

Table XXI

Delta (δ) Angles between Normals to Planes for $La(DFBPSC)(NO_3)_3 \cdot 3H_2O$

Edge	Observed Angle	MCPAP	Δ	DHH	Δ	2-6-3	Δ
N(11)-N(12)	63.32	45.15	18.17	61.41	1.91	65.85	2.53
N(11)-N(21)	62.02	40.92	21.10	61.33	0.69	65.85	3.83
N(11)-O(1)	35.34	43.22	7.88	27.59	7.75	29.73	5.61
N(11)-O(2)	18.46	45.15	26.69	27.59	9.13	29.73	11.27
N(11)-O(4)	35.42	40.91	5.49	27.48	7.94	27.83	7.59
N(11)-O(5)	15.39	0.0	15.39	27.48	12.09	27.83	12.44
N(12)-O(1)	47.43	43.22	4.23	54.86	7.41	54.05	6.60
N(12)-O(5)	56.41	40.92	15.49	54.86	1.55	72.85	16.44
N(12)-O(11)	56.01	45.16	10.85	44.90	11.11	24.74	31.27
N(21)-O(2)	58.84	40.92	17.92	54.83	4.01	54.05	4.79
N(21)-O(4)	43.59	76.11	32.52	54.83	11.24	72.85	29.26
N(21)-N(22)	59.07	76.11	17.04	44.95	14.12	24.74	34.33
O(1)-O(2)	65.27	43.22	22.05	60.88	4.39	55.53	9.74
O(1)-O(11)	35.08	43.22	8.14	36.94	1.86	22.60	12.48
O(1)-O(w1)	35.72	43.22	7.50	41.94	6.22	46.05	10.33

O(2)-N(22)	26.54	40.92	14.38	36.88	10.34	22.60	3.94
O(2)-O(w1)	47.83	45.15	2.68	41.91	5.92	46.05	1.78
O(4)-O(5)	67.87	76.11	8.24	60.88	6.99	22.60	21.68
O(4)-N(22)	38.37	0.0	38.37	36.88	1.49	46.05	34.48
O(4)-O(21)	24.33	0.0	24.33	41.91	17.58	46.19	3.50
O(5)-O(11)	37.66	40.92	3.26	36.94	0.72	72.85	35.19
O(5)-O(21)	48.20	76.11	27.91	41.94	6.26	27.83	20.37
N(22)-O(w1)	44.03	40.92	3.11	48.57	4.54	36.20	7.83
N(22)-O(21)	57.13	76.11	18.98	48.57	8.56	67.94	10.81
O(11)-O(w1)	52.22	45.15	7.07	48.54	3.68	36.21	16.01
O(11)-O(21)	41.82	40.92	0.90	48.54	6.72	67.94	26.12
O(w1)-O(21)	44.99	40.92	4.07	36.29	8.70	54.45	9.46
Root-Mean-Squared $\Delta = \left(\frac{\Sigma\Delta^2}{n}\right)^{\frac{1}{2}}$			17.26		7.96		17.90

Table XXII

Comparison of Atom Coordinates and Ideal Coordinates
Using Dollase's Method for $Eu(DFBPSC)(NO_3)_3 \cdot 2H_2O$

		Atom Coordinates	BCSAP	Δ	DTH	Δ	2-6-2	Δ
N(21)	x	1.2717	1.4779	-0.2062	1.1892	0.0824	0.9892	0.2825
	y	2.1313	2.0067	0.1246	2.1373	-0.0060	2.1415	-0.0102
	z	0.7226	0.1304	0.5922	0.4292	0.2934	0.8644	-0.1418
O(3)	x	2.1260	2.1680	-0.0419	1.9305	0.1955	1.8989	0.2271
	y	-0.8012	-0.9505	0.1493	-1.2052	0.4040	-0.9666	0.1654
	z	-1.1244	-0.7901	-0.3343	-1.0888	-0.0356	-1.2715	0.1471
O(21)	x	0.2813	0.0779	0.2034	0.0664	0.2149	0.8365	-0.5552
	y	-2.0836	-2.1021	0.0186	-1.9146	-0.1690	-2.1602	0.0766
	z	1.3409	1.3427	-0.0018	1.5276	-0.1867	0.8613	0.4796
O(4)	x	-0.9182	-0.6122	-0.3061	-0.4970	-0.4213	-0.8586	-0.0597
	y	0.6983	0.8550	-0.1567	0.7472	-0.0488	0.5717	0.1267
	z	2.1673	2.2632	-0.0959	2.3125	-0.1452	2.2675	-0.1002
N(11)	x	-1.0880	-1.2658	0.1778	-1.4624	0.3743	-0.8365	-0.2515
	y	2.2480	2.1387	0.1093	1.9653	0.2827	2.1602	0.0878
	z	-0.6147	-0.0857	-0.5291	-0.0545	-0.5603	-0.8613	0.2466
O(6)	x	-2.1916	-2.2557	0.0641	-2.3064	0.1147	-2.2322	0.0406
	y	-0.5834	-0.7665	0.1831	-0.6454	0.0620	-0.4643	-0.1192
	z	1.0483	0.7715	0.2768	0.6459	0.4024	1.0035	0.0448
O(11)	x	-0.4809	-0.2900	-0.1910	-0.5663	0.0854	-0.9892	0.5083
	y	-2.0368	-2.0432	0.0064	-2.1599	0.1231	-2.1415	0.1047
	z	-1.3711	-1.3874	0.0163	-1.0865	-0.2845	-0.8644	-0.5067

O(1)	x	0.9715	0.6999	0.2716	1.0230	-0.0514	1.1919	-0.2204
	y	0.6445	0.8620	-0.2176	1.0980	-0.4535	0.8592	-0.2148
	z	-2.1758	-2.2446	0.0688	-2.0280	-0.1478	-1.9995	-0.1762
N(12)	x	-1.9907	-1.8243	-0.1664	-1.4570	-0.5337	-1.8257	-0.1650
	y	0.0167	0.1120	-0.0953	0.1006	-0.0840	0.0187	-0.0020
	z	-1.6149	-1.7273	0.1124	-2.0083	0.3934	-1.7257	0.1108
N(22)	x	2.0191	1.8243	0.1948	2.0800	-0.0608	1.8257	0.1934
	y	-0.2336	-0.1120	-0.1217	-0.1233	-0.1104	-0.0187	-0.2149
	z	1.6218	1.7273	-0.1055	1.3509	0.2709	1.7257	-0.1039
Root-mean-square del = $\left(\frac{\Delta^2}{n}\right)^{\frac{1}{2}}$				0.2181		0.2701		0.2387

Table XXIII

Comparison of Atomic Coordinates and Ideal Coordinates
Using Dollase's Method for $La(DFBPSC)(NO_3)_3 \cdot 3H_2O$

		Atom Coordinates	DHH	Δ	MCPAP	Δ	2-6-3	Δ
N(11)	x	-0.5344	-0.5166	-0.0179	-0.8563	0.3219	-0.5779	0.0434
	y	2.0259	2.0958	-0.0699	1.2765	0.7494	1.9794	0.0464
	z	-1.6593	-1.6099	-0.0495	-1.9354	0.2761	-1.6078	-0.0516
N(12)	x	-1.8315	-1.8998	0.0683	-1.4450	-0.3865	-1.5175	-0.3140
	y	1.8821	1.7743	0.1077	1.9957	-0.1136	1.7212	0.1608
	z	0.7321	0.5523	0.1798	0.7187	0.0134	0.4984	0.2337
N(21)	x	1.2985	1.3690	-0.0704	1.9242	-0.6257	1.2556	0.0429
	y	0.1470	0.3794	-0.2323	0.2717	-0.1247	0.5862	-0.4392
	z	-2.3617	-2.2067	-0.1550	-1.8364	-0.5253	-1.8957	-0.4660
O(1)	x	-2.4323	-2.5687	0.1365	-2.6045	0.1722	-2.3465	-0.0857
	y	-0.5324	-0.5852	0.0528	-0.3199	-0.2125	-0.7906	0.2582
	z	-0.9473	-0.6074	-0.3399	-0.4910	-0.4563	-0.9746	0.0273
O(2)	x	-0.8468	-0.6710	-0.1758	-0.4847	-0.3622	-1.1111	0.2643
	y	-1.4166	-1.3930	-0.0236	-1.3788	-0.0379	-1.2963	-0.1204
	z	-2.0900	-2.2114	0.1214	-2.1790	0.0890	-2.0411	-0.0488
O(4)	x	2.1057	2.4208	-0.3151	1.3779	0.7278	2.6285	-0.5228
	y	1.4161	1.1825	0.2336	2.1932	-0.7771	0.7671	0.6491
	z	0.1975	0.1494	0.0481	-0.1859	0.3834	-0.5276	0.7251
O(5)	x	0.7625	0.5231	0.2394	1.0462	-0.2837	-0.2678	1.0303
	y	1.8186	1.9904	-0.1718	1.3443	0.4743	1.9525	-0.1338
	z	1.8553	1.7534	0.1018	2.1212	-0.2659	1.9728	-0.1176

N(22)	x	2.1708	1.8585	0.3123	1.9318	0.2391	2.1494	0.0214
	y	-1.5302	-1.7564	0.2261	-1.7651	0.2349	-1.0652	-0.4650
	z	-0.4818	-0.5179	0.0361	-0.5493	0.0675	-0.0775	-0.4043
O(11)	x	-1.5444	-1.3272	-0.2172	-1.4368	-0.1076	-0.6237	-0.9206
	y	-0.2357	-0.3980	0.1623	-0.2152	-0.0205	0.0698	-0.3054
	z	2.2000	2.1723	0.0277	2.1158	0.0842	2.3166	-0.1166
O(w1)	x	-0.5821	-0.6372	0.0550	-0.8431	0.2609	-0.7986	0.2165
	y	-2.5501	-2.5138	-0.0362	-2.3005	-0.2496	-2.6006	0.0505
	z	0.5836	0.4665	0.1171	0.3250	0.2587	0.3078	0.2758
O(21)	x	1.4341	1.4490	-0.0149	1.3902	0.0439	1.2097	0.2243
	y	-1.0246	-0.7760	-0.2486	-1.1020	0.0774	-1.3234	0.2989
	z	1.9718	2.0594	-0.0877	1.8964	0.0753	2.0287	-0.0569
Root-mean-squared Del = $\left(\frac{\Delta^2}{n}\right)$				0.1640		0.3488		0.3764

CHAPTER FOUR

THE CRYSTAL AND MOLECULAR STRUCTURE OF 1,4-DIHYDRAZINOPHTHALAZINEBIS(2-PYRIDINE CARBOXALDIMINE)TRIHYDRATE

Binuclear ligands are ligands that are capable of binding two metal ions in close proximity. Binuclear complexes are of interest because of their unusual magnetic properties,[128-130] their chemical reactivity,[131,132] and as model systems for nitrogen fixing enzymes.[133,134] Synthetic routes to such complexes have been the subject of some recent reviews.[135,136] In view of the wealth of chemistry in such systems and our interest in multidentate ligands, 1,4-dihydrazinophthalazinebis(2-pyridine carboxaldimine) (DHPHPY) was synthesized. This ligand has two cavities, each capable of binding to a metal ion. The metal ions could be linked by a bridging ligand. That DHPHPY is capable of coordinating to two metal ions simultaneously was shown by the synthesis and crystal structure determination of $[Ni_2Cl(H_2O)_4DHPHPY]$-$Cl_3 \cdot 2H_2O$ in this laboratory.[137] The attempt to synthesize and structurally characterize the analogous Mn(II) complex is the subject of this chapter.

Structural Solution and Refinement for $DHPHPY \cdot 3H_2O$

Solid $MnCl_2 \cdot 4H_2O$ was added in a 2:1 mol ratio to an ethanol solution of DHPHPY. The resulting solid was

dissolved in a water-ethanol solution. Crystals suitable for X-ray diffraction studies were obtained by slow evaporation of this orange solution. The measured density (1.36 g/cc) was low for the expected dimanganese complex which suggested that no metal ion was coordinated to the ligand. Subsequent X-ray analysis proved this to be the case.

From the precession photographs, the space group was found to be $P2_1/c$. From the measured density and volume of the cell, there was one molecule of DHPHPY and three molecules of water per asymmetric unit.

The MULTAN package of programs was used to assign probable phase values to 300 of the largest E's. From the phase set with the largest combined figures of merit, an E-map was calculated which revealed all 28 atoms of the ligand. Subsequent Fourier syntheses revealed the three water molecules. The R value at this stage was 21.3%. Three cycles of least-squares refinement with isotropic temperature parameters were applied to all atoms during three additional cycles of least-squares after which the R value was lowered to 7.4%. A difference Fourier map was calculated and sensible positions for all 22 hydrogen atoms were found. The hydrogen atoms were assigned an isotropic thermal parameter and were used in, but not refined during, the final three cycles of least-squares refinement. The final R value was 6.3%.

Results and Discussion

An ORTEP[71] drawing of the compound DHPHPY·$3H_2O$ with the atomic numbering scheme is shown in Figure 10. The final positional and thermal parameters are listed in Table XXIV and Table XXV, respectively. Bond distances and angles are listed in Table XXVI and Table XXVII, respectively.

The fact that no Mn(II) ion was coordinated by the ligand was unexpected. Steric effects can be ruled out in view of the similarity in the crystal radii of Ni(II) and Mn(II),[43] and the results obtained with 1,4-dihydrazinophthalazinebis(2-pyridinium carboxaldimine)nitrate dihydrate [H_2DHPHPY$(NO_3)_2$·$2H_2O$].[137] Apparently the ligand cannot compete effectively with the water molecules of the solvent for donor sites on Mn(II).

In the absence of coordination to a metal, the N atoms of the ligand can hydrogen-bond to water molecules as was observed in H_2DHPHPY$(NO_3)_2$·$2H_2O$.[137] Structural analysis of DHPHPY·$3H_2O$ showed two water molecules, O(1) and O(3), hydrogen-bonded to some of the N atoms of the ligand, with a third water molecule, O(2), acting as a bridging ligand between them. Table XXVIII lists the hydrogen-bond distances along with the donor-hydrogen atom-acceptor angles (DH···A). These distances are similar to those observed in H_2DHPHPY$(NO_3)_2$·$3H_2O$ which had an average hydrogen-bond distance of 2.80 Å.[137]

The mode of coordination of the water molecules in DHPHPY·$3H_2O$ is in some respects similar to that found in $(Ni_2Cl(H_2O_4$DHPHPY$)Cl_3$·$2H_2O$ where two Ni(II) ions were located

Figure 10

ORTEP Drawing and Atomic Numbering Scheme for DHPHPY·$3H_2O$

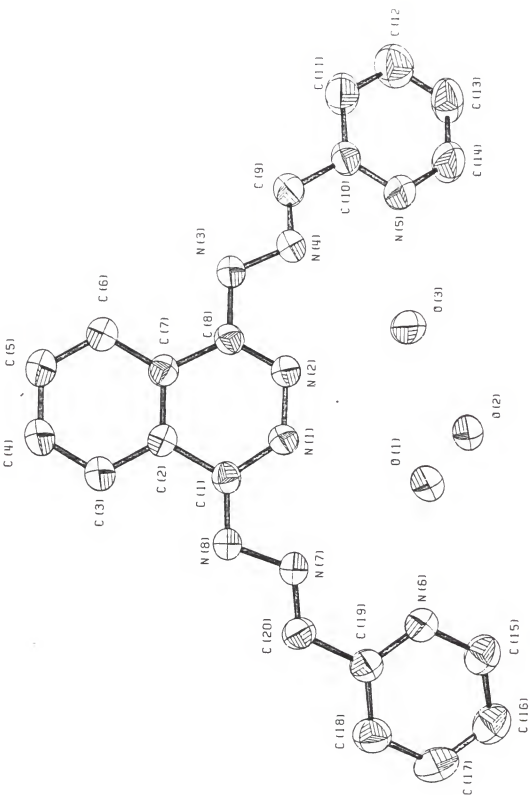

C(5)
C(6)
C(7)
C(8)
N(3)
C(4)
N(2)
C(9)
N(4)
C(11)
C(12)
C(3)
C(2)
C(1)
N(1)
C(10)
C(13)
O(3)
N(5)
C(14)
O(2)
O(1)
N(8)
N(7)
C(20)
C(19)
N(6)
C(18)
C(15)
C(16)
C(17)

Table XXIV

Final Positional Parameters for Non-hydrogen Atoms for DHPHPY·$3H_2O$[a]

ATOM	X	Y	Z
C(1)	-1180(3)	998(2)	3325(2)
C(2)	-3975(3)	453(2)	3602(2)
C(3)	-3798(3)	2057(2)	4543(2)
N(1)	257(3)	1675(2)	5062(2)
N(2)	-673(3)	2290(2)	5352(2)
N(3)	-1147(3)	3370(2)	6384(2)
N(4)	-2526(3)	3411(2)	5941(2)
N(5)	-5422(4)	3497(2)	5216(2)
N(6)	483(3)	-451(2)	2869(2)
N(7)	1678(3)	415(2)	4423(2)
N(8)	2352(3)	815(2)	5215(2)
C(1)	1551(4)	1448(2)	5595(2)
C(2)	2045(4)	1963(2)	6327(2)
C(3)	3392(4)	1809(3)	6823(3)
C(4)	3845(4)	2311(3)	7590(3)
C(5)	2995(5)	2983(3)	7857(3)
C(6)	1664(4)	3144(3)	7384(3)
C(7)	1173(4)	2629(2)	6612(2)
C(8)	-235(4)	2740(2)	6088(2)
C(9)	-3381(4)	3919(3)	6300(3)
C(10)	-4872(4)	4038(3)	5903(2)
C(11)	-5671(5)	4707(3)	6236(3)
C(12)	-7084(5)	4812(4)	5870(4)
C(13)	-7641(5)	4278(4)	5168(3)
C(14)	-6794(5)	3627(3)	4872(3)
C(15)	-69(5)	-903(3)	2119(3)
C(16)	648(5)	-1584(3)	1738(3)
C(17)	1971(5)	-1825(3)	2146(3)
C(18)	2567(4)	-1367(3)	2927(3)
C(19)	1796(4)	-683(2)	3270(2)
C(20)	2405(4)	-194(3)	4094(2)

[a]All values x 10^4.

Table XXV

Final Temperature Parameters for Non-hydrogen Atoms for DHPHPY·$3H_2O$[a]

ATOM	U11	U22	U33	U12	U13	U23
C(1)	46(1)	53(2)	48(1)	4(1)	-2(1)	1(1)
C(2)	67(1)	66(2)	54(2)	6(1)	-9(1)	-1(1)
C(3)	60(2)	70(2)	84(2)	14(1)	-17(1)	-27(2)
N(1)	40(1)	45(2)	37(2)	6(1)	2(1)	-1(1)
N(2)	44(1)	45(2)	37(2)	6(1)	5(1)	-1(1)
N(3)	45(1)	51(2)	43(2)	9(1)	-5(1)	-9(1)
N(4)	46(1)	47(2)	43(2)	7(1)	-5(1)	0(1)
N(5)	54(2)	59(2)	53(2)	9(1)	-2(1)	-7(2)
N(6)	48(1)	49(2)	42(2)	9(1)	4(1)	-6(1)
N(7)	42(1)	47(2)	37(2)	1(1)	-2(1)	-3(1)
N(8)	40(1)	50(2)	41(2)	4(1)	-3(1)	-8(1)
C(1)	38(2)	43(2)	33(2)	0(1)	2(1)	2(1)
C(2)	41(2)	39(2)	37(2)	-3(1)	2(1)	-2(1)
C(3)	43(2)	67(3)	56(2)	6(2)	-6(2)	-17(2)
C(4)	44(2)	77(3)	65(3)	7(2)	-13(2)	-21(2)
C(5)	53(2)	62(3)	56(3)	-1(2)	-8(2)	-18(2)
C(6)	47(2)	48(2)	51(2)	0(2)	-1(2)	-8(2)
C(7)	42(2)	37(2)	36(2)	-1(1)	2(1)	2(1)
C(8)	40(2)	39(2)	36(2)	3(1)	2(1)	3(1)
C(9)	56(2)	57(2)	45(2)	17(2)	-4(1)	-7(2)
C(10)	51(2)	55(2)	39(2)	11(2)	0(1)	0(2)
C(11)	61(2)	95(3)	59(3)	27(2)	-3(2)	-19(2)
C(12)	64(3)	89(4)	74(3)	28(3)	6(2)	-3(3)
C(13)	47(2)	95(4)	55(3)	15(2)	-2(2)	0(2)
C(14)	52(2)	77(3)	60(3)	3(2)	-6(2)	-5(2)
C(15)	58(2)	60(3)	47(2)	-12(2)	3(2)	-10(2)
C(16)	68(3)	60(3)	49(3)	-11(2)	6(2)	-15(2)
C(17)	76(3)	47(3)	61(3)	-1(2)	24(2)	-13(2)
C(18)	55(2)	50(2)	56(2)	4(2)	9(2)	-5(2)
C(19)	44(2)	40(2)	39(2)	-1(1)	8(1)	1(1)
C(20)	49(2)	44(2)	40(2)	4(1)	7(1)	-2(1)

[a]All values x 10^4.

Table XXVI

Bond Distances for DHPHPY·$3H_2O$ (Å)

N(1)-C(1)	1.352(4)	N(2)-C(8)	1.296(4)
C(1)-C(2)	1.460(5)	C(7)-C(8)	1.458(5)
C(2)-C(3)	1.400(50	C(6)-C(7)	1.400(5)
C(3)-C(4)	1.377(6)	C(5)-C(6)	1.376(6)
N(8)-C(1)	1.317(5)	N(3)-C(8)	1.384(5)
N(7)-N(8)	1.388(4)	N(3)-N(4)	1.379(4)
N(7)-C(20)	1.274(5)	N(4)-C(9)	1.268(5)
C(20)-C(19)	1.468(5)	C(9)-C(10)	1.463(6)
N(6)-C(19)	1.349(5)	N(5)-C(10)	1.347(5)
N(6)-C(15)	1.341(5)	N(5)-C(14)	1.342(6)
C(15)-C(16)	1.382(6)	C(14)-C(13)	1.367(7)
C(16)-C(17)	1.363(7)	C(13)-C(12)	1.358(7)
C(17)-C(18)	1.393(6)	C(12)-C(11)	1.380(7)
C(18)-C(19)	1.388(5)	C(11)-C(10)	1.382(6)
N(1)-N(2)	1.377(4)		
C(2)-C(7)	1.392(5)		
C(4)-C(5)	1.376(6)		

Table XXVII

Bond Angles for DHPHPY·$3H_2O$

N(2)-N(1)-C(1)	126.3(3)	N(1)-N(2)-C(8)	117.3(3)
N(1)-C(1)-N(8)	123.1(3)	N(2)-C(8)-N(3)	118.2(3)
N(1)-C(1)-C(2)	116.0(3)	N(2)-C(8)-C(7)	123.6(3)
N(8)-C(1)-C(2)	120.9(3)	N(3)-C(8)-C(7)	118.2(3)
C(1)-C(2)-C(3)	121.1(3)	C(8)-C(7)-C(6)	123.4(3)
C(1)-C(2)-C(7)	119.3(3)	C(8)-C(7)-C(2)	117.2(3)
C(3)-C(2)-C(7)	119.6(3)	C(6)-C(7)-C(2)	119.4(3)
C(2)-C(3)-C(4)	120.1(4)	C(7)-C(6)-C(5)	119.9(4)
C(3)-C(4)-C(5)	120.2(4)	C(6)-C(5)-C(4)	120.8(4)
C(1)-N(8)-N(7)	111.2(3)	C(8)-N(3)-N(4)	117.9(3)
N(8)-N(7)-C(20)	114.6(3)	N(3)-N(4)-C(9)	116.2(3)
N(7)-C(20)-C(19)	119.9(3)	N(4)-C(9)-C(10)	122.4(4)
N(6)-C(19)-C(20)	118.2(3)	N(5)-C(10)-C(9)	119.0(4)
N(6)-C(19)-C(18)	121.8(3)	N(5)-C(10)-C(11)	121.9(4)
C(20)-C(19)-C(18)	120.0(3)	C(9)-C(10)-C(11)	119.1(4)
C(19)-C(18)-C(17)	119.3(4)	C(10)-C(11)-C(12)	119.1(4)
C(18)-C(17)-C(16)	118.8(4)	C(11)-C(12)-C(13)	119.3(5)
C(17)-C(16)-C(15)	119.1(4)	C(12)-C(13)-C(14)	118.6(5)
C(16)-C(15)-N(6)	123.2(4)	C(13)-C(14)-N(5)	123.8(4)
C(15)-N(6)-C(19)	117.8(3)	C(14)-N(5)-C(10)	117.1(4)

Table XXVIII

Hydrogen-Bonding Distances and Angles for DHPHPY·$3H_2O$

D-H···A	Distance	Angle
N(1)-H(n1)···O(1)	2.913(4)	166.5(2)
O(1)-H(w1)···N(6)	2.814(4)	155.3(2)
O(1)-H(w2)···O(2)	2.830(4)	172.3(2)
O(2)-H(w3)···N(8)*	2.888(4)	160.6(2)
O(2)-H(w4)···O(3)	2.778(4)	166.8(2)
O(3)-H(w5)···N(5)	2.894(5)	171.0(2)
O(3)-H(w6)···N(2)	3.054(5)	160.8(2)
N(3)-H(w3)···O(1)†	2.997(4)	167.4(2)

*N(8) translated -x,-y,1-z.

†O(1) translated x,½-y,½+z.

in the cavity with a chloride ion bridge.[137] In the latter complex, however, the ligand was planar and the Ni(II) ions both less than 0.10 Å out of the least-squares plane of the ligand.[137] In this present complex, the ligand is not flexible enough to allow the cavity to expand and accommodate the two bridged water molecules and still remain planar. The distortion from planarity is substantial. Deviations from the least-squares plane through DHPHPY range from -1.09 Å for atom C(16) of pyridine ring II to 0.46 Å for C(6) of the phthalazine ring system. The largest deviation from planarity for the oxygen atoms is -2.06 Å for atom O(2). These values and the least-squares planes through various sections of the ligand and pertinent dihedral angles between these planes are listed in Table XXIX. The phthalazine ring system is very close to being planar with the largest deviation from the least-squares plane being 0.05 Å for atom N(1). In the previous two studies the largest deviation from planarity was 0.02 Å. The unsubstituted molecule 2,3-diazanaphthalene was found to be planar.[138] Sidearm II and pyridine ring II are planar. Sidearm I and pyridine ring I are not completely planar with atom C(9) being 0.08 Å out of the least-squares plane through atoms N(3), N(4), N(5) and C(9) through C(14). The large deviation from planarity for the ligand as a whole is the result of a rotation about the C(8)-N(3) bond joining sidearm I to the phthalazine ring system. The dihedral angle between the least-squares plane through sidearm I and pyridine ring I

and the least-squares plane through the phthalazine ring system is 9.3°. Sidearm II and pyridine ring II are coplanar with the phthalazine ring system.

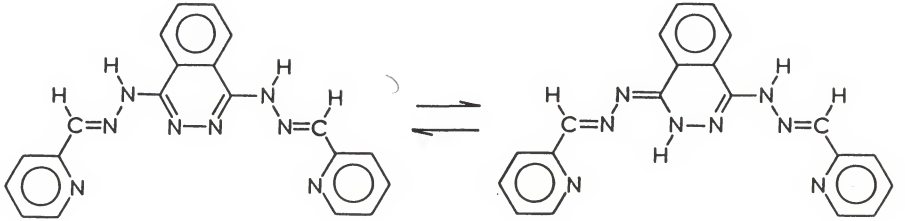
In addition to the non-planarity of DHPHPY, a number of other significant differences are observed in this present study relative to the two earlier structure determinations. Unlike H_2DHPHPY$(NO_3)_2 \cdot 2H_2O$[137] which has an exact two-fold rotational axis and the Ni(II) complex[137] which has approximate two-fold symmetry , DHPHPY$\cdot 3H_2O$ has no such symmetry axis. The bond distance between atom C(1) of the phthalazine ring system and atom N(8) of sidearm II is 1.317(5) Å, which is close to the expected distance of 1.28 Å for a carbon-nitrogen double bond.[52] By contrast, the bond distance between atom C(8) of the phthalazine moiety and atom N(3) of sidearm I is 1.384(5) Å. The latter bond distance is closer to that found for the analogous bonds in the two earlier studies. In the Ni(II) complex, these distances are 1.370(8) Å and 1.382(8) Å.[137] For H_2DHPHPY$(NO_3)_2 \cdot 2H_2O$, the bond distance is 1.362(4) Å.[137] There are differences in the carbon-nitrogen bond distances in the phthalazine ring system. The distance between atom C(1) and atom N(1) is 1.352(4) Å. The difference between atom C(8) and atom N(2) is 1.296(4) Å which is close to the bond distances found for the analogous atoms in H_2DHPHPY$(NO_3)_2 \cdot 2H_2O$ and in the Ni(II) complex.[137] In the former complex this distance amounts to 1.318(4) Å while in the latter complex these distances are 1.302(8) Å and 1.313(8) Å. These large differences in bond

distances are due to the fact that DHPHPY exists in a different tautomeric form in this present complex than it did in the two earlier studies. Figure 11 shows the equilibrium between the two tautomeric forms observed for this ligand. The proton that was bound to atom N(8) in the Ni(II) complex and in H_2DHPHPY is transferred to atom N(1) of the phthalazine ring system. The bonding distances suggest the formation of a carbon-nitrogen double bond between atoms N(8) and C(1) and a single bond between atoms C(1) and N(1). The hydrogen atom H(N1) is within normal hydrogen-bonding distance to atom O(1). The hydrogen atom positional parameters and the atoms to which they are bound, along with the bonding distances, are shown in Table XXX. The observation of a different tautomer than was found for $H_2DHPHPY(NO_3)_2 \cdot 2H_2O$ suggests that there is little energy difference between the two tautomeric forms. The energy difference cannot amount to much more than that obtained by the formation of a hydrogen bond. The ease with which proton transfers can take place in protonic solvents like water suggests that there is likely a large percentage of this compound in the form of tautomer II in solution.

The observed deviation from planarity in $DHPHPY \cdot 3H_2O$ is likely due to the steric requirements resulting from coordination by three water molecules. Table XXXI lists the cavity sizes of the ligand DHPHPY in the three compounds. It can be seen from this table that the cavity size for $H_2DHPHPY(NO_3)_2 \cdot 2H_2O$ is only slightly smaller than that found for $DHPHPY \cdot 3H_2O$.

Figure 11

Illustration of Tautomeric Forms Observed for DHPHPY



Tautomer I

Tautomer II

The ligand in the former complex is planar, and it is possible that this represents an upper limit on the cavity size for the ligand before a deviation from planarity will occur. The cavity found for the Ni(II) complex is much smaller than that found for the other two complexes. This is due to a much stronger interaction between the Ni(II) ions and the N donors of the ligand. It is also an indication of the flexibility of the ligand in accommodating ions of various sizes.

The failure to isolate a Mn(II) complex with DHPHPY and similar failures for some other first-row transition metal ions was unexpected.[137] Difficulty in isolating a metal complex may be due to an abundance of tautomer II (Figure 11) in solution. Tautomer II, with N(1) protonated, would be less likely to coordinate to a metal ion. This possibility plus the large excess of water molecules is likely the reason for the many failures. Any future work with DHPHPY should probably be performed in non-coordinating solvent systems.

Table XXIX

Least-Squares Planes and Selected Dihedral for DHPHPY·$3H_2O$

LEAST-SQUARES PLANES

Plane 1			Pyridine Ring I			
Defined by Atoms	N(5)	C(10)	C(11)	C(12)	C(13)	C(14)
Deviation (Å)	0.0	-0.002	0.008	-0.012	-0.012	-0.004
Plane 2			Sidearm I			
Defined by Atoms	N(5)	C(10)	C(11)	C(12)	C(13)	C(14)
Deviation (Å)	-0.043	-0.043	0.007	0.025	0.045	-0.010
	N(3)	N(4)	C(9)			
	0.027	0.073	-0.082			
Plane 3			Pyridine Ring II			
Defined by Atoms	N(6)	C(15)	C(16)	C(17)	C(18)	C(19)
Deviation (Å)	0.001	-0.005	0.006	-0.003	-0.001	0.002
Plane 4			Sidearm II			
Defined by Atoms	N(6)	C(15)	C(16)	C(17)	C(18)	C(19)
Deviation (Å)	0.011	-0.005	-0.005	-0.014	-0.001	0.013
	N(7)	N(8)	C(20)			
	-0.003	-0.022	0.025			

Plane 5 — Phthalazine Ring System

Defined by Atoms	N(1)	N(2)	C(1)	C(2)	C(3)	C(4)
Deviation (Å)	0.053	-0.012	0.001	-0.015	-0.019	-0.017
	C(5)	C(6)	C(7)	C(8)		
	0.029	0.026	-0.001	-0.042		

DIHEDRAL ANGLES(°)

Plane 1 - Plane 2	1.9
Plane 1 - Plane 5	8.2
Plane 2 - Plane 4	9.8
Plane 2 - Plane 5	9.3
Plane 3 - Plane 4	0.5
Plane 3 - Plane 5	0.8
Plane 4 - Plane 5	0.6

Table XXX

Atomic Positional Parameters and Bond Distances for Hydrogen Atoms in DHPHPY·$3H_2O$

Atom [Bonded to]	Distance (Å)	x	y	z
			($\times 10^4$)	
H(n1)[N(1)]	0.88	-63	1392	4548
H(n3)[N(3)]	0.98	-1006	3595	7016
H(3)[C(3)]	1.02	4017	1310	6625
H(4)[C(4)]	0.97	4783	2235	7934
H(5)[C(5)]	1.06	3354	3351	8454
H(6)[C(6)]	1.05	1065	3697	7544
H(9)[C(9)]	1.05	-3012	4265	6903
H(11)[C(11)]	1.02	-5210	5061	6787
H(12)[C(12)]	1.11	-7673	5407	6065
H(13)[C(13)]	0.96	-8607	4338	4848
H(14)[C(14)]	1.03	-7229	3176	4384
H(15)[C(15)]	1.05	-1085	-686	1836
H(16)[C(16)]	1.01	112	-1902	1196
H(17)[C(17)]	1.05	2601	-2376	2029
H(18)[C(18)]	1.08	3575	-1566	3307
H(20)[C(20)]	1.01	3385	-362	4409
H(w1)[O(1)]	0.98	-701	425	3323
H(w2)[O(1)]	0.94	-2118	793	3364
H(w3)[C(2)]	0.97	-3619	32	4074
H(w4)[O(2)]	0.91	-4041	953	3949
H(w5)[O(3)]	1.05	-4402	2537	4842
H(w6)[O(3)]	0.93	-2934	2106	4919

Table XXXI

Cavity Sizes for DHPHPY (Å)

	DHPHPY·$3H_2O$	$Ni_2Cl(H_2O)_4$DHPHPY-$(NO_3)_2$·$2H_2O$	H_2DHPHPY-$(NO_3)_2$·$2H_2O$
N(1)-N(7)	2.563	2.531	2.599
N(2)-N(4)	2.646	2.521	2.599
N(7)-N(6)	2.742	2.620	2.706
N(4)-N(5)	2.804	2.583	2.706
N(1)-N(6)	4.557	4.056	4.552
N(2)-N(5)	4.805	4.045	4.552
N(6)-N(5)	9.093	7.116	8.880

REFERENCES

1. M. G. B. Drew. Coord. Chem. Rev. 24, 179 (1977).

2. B. E. Robertson. Inorg. Chem. 16, 2735 (1977).

3. S. P. Sinha. Struct. Bond. 25, 69 (1976).

4. J. E. Huheey. "Inorganic Chemistry: Principles of Structure and Reactivity," 2nd Ed., Harper and Row, New York, 1978.

5. A. P. Ginsberg. Inorg. Chem. 3, 558 (1964).

6. S. C. Abrahams and A. P. Ginsberg. Inorg. Chem. 3, 558 (1964).

7. D. W. Wester and G. J. Palenik. J. Am. Chem. Soc. 96, 7566 (1974).

8. T. J. Giordano, G. J. Palenik, R. C. Palenik, and D. A. Sullivan. Inorg. Chem. 18, 2445 (1979).

9. J. H. Davis, G. J. Palenik, and R. C. Palenik. "Pentagonal Bipyramidal Complexes of Cd(II) and Hg(II)," presented at the 181st American Chemical Society National Meeting, Atlanta, March 1981.

10. J. E. Thomas and G. J. Palenik. Inorg. Chim. Acta Let. 44, L303 (1980).

11. J. E. Thomas, R. C. Palenik, and G. J. Palenik. Inorg. Chim. Acta 37, L459 (1979).

12. S. J. Lippard. Prog. Inorg. Chem. 8, 130 (1967).

13. N. K. Dalby, M. H. Muellar, and S. H. Simonsen. Inorg. Chem. 10, 323 (1971).

14. G. Marangoni, S. Degetto, R. Granziani, G. Bombieri, and E. Forsellini. J. Inorg. Nucl. Chem. 36, 1787 (1974).

15. J. de O. Cabral, M. F. Cabral, W. J. Cummings, M. G. B. Drew, A. Rodgers, and S. M. Nelson. Inorg. Chim. Acta Let. 30, L313 (1978).

16. M. G. B. Drew, J. de O. Cabral, F. S. Esko, and S. M. Nelson. J. Chem. Soc. Chem. Comm. 22, 1033 (1979).

17. W. Radecka-Paryzek. Inorg. Chim. Acta Let. 45, L147 (1980).

18. E. L. Muetterties and C. M. Wright. Quart. Rev. Chem. Soc. 21, 209 (1967).

19. J. L. Hoard and J. V. Silverton. Inorg. Chem. 2, 235 (1963).

20. J. K. Burdette, R. Hoffman, and R. C. Fay. Inorg. Chem. 17, 2553 (1978).

21. W. L. Jolly. "The Synthesis and Characterization of Inorganic Compounds," Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1970.

22. S. C. Watson and J. E. Eastham, J. Org. Met. Chem. 9, 165 (1967).

23. Chem. Abs. 49, 7606e (1955). British patent no. 707337.

24. J. E. Parks, B. E. Wagner, and R. H. Holm. J. Orgomet. Chem. 56, 53 (1973).

25. R. T. Conley. "Infrared Spectroscopy," 2nd Ed., Allyn and Bacon, Inc., Boston, Massachusetts, 1972.

26. J. E. Thomas. Thesis, University of Florida (1980).

27. M. Mashima. Bull. Soc. Chem. Japan 37, 974 (1964).

28. K. Nakamoto. "Infrared Spectra of Inorganic and Coordination Compounds," 3rd Ed., John Wiley and Sons, New York, 1978.

29. M. J. Buerger. "The Precession Method," John Wiley and Sons, New York, 1964.

30. U. W. Arndt and B. T. M. Willis. "Single Crystal Diffractometry," The University Press, Cambridge, 1966.

31. A. J. C. Wilson. Nature 150, 151 (1942).

32. A. J. C. Wilson, Acta. Cryst. 2, 318 (1949).

33. E. R. Howells, D. C. Phillips, and D. Rogers, Acta Cryst. 3, 210 (1950).

34. G. H. Stout and L. H. Jensen. "X-Ray Structure Determination," The Macmillan Company, New York, 1968.

35. "International Tables for X-ray Crystallography," Volume IV, J. A. Ibers and W.C. Hamilton, Eds., The Kynoch Press, Birmingham, 1974.

36. P. Main, S. E. Hull, L. Lessinger, G. Germain, J.-P. DeClercq, and M. M. Woolfson. "MULTAN 78: A Computer Program for the Automatic Solution of Crystal Structures," University of York, York, England, 1978.

37. J. Karle and H. Hauptman. Acta Cryst. 9, 635 (1956).

38. M. M. Woolfson. "Direct Methods in Crystallography," Oxford University Press, London, 1961.

39. G. Germain, P. Main, and M. M. Woolfson. Acta Cryst. A27, 368 (1971).

40. I. L. Karle, H. Hauptman, J. Karle, and A. B. Wing. Acta Cryst. 11, 257 (1958).

41. J. H. Davis and G. J. Palenik, private communication.

42. H. Aghaborzorg, Dissertation, University of Florida (1982).

43. R. D. Shannon. Acta Cryst. A32, 751 (1976).

44. T. Moellar. "The Chemistry of the Lanthanides," Rheinhold, New York (1963).

45. T. Moellar. M. T. P. Inter. Rev. Sci. 7, 275 (1972).

46. R. G. Pearson. "Hard and Soft Acids and Bases," Dowden, Hutchinson and Ross, Inc., Stroudsberg (1973).

47. J. A. Glasel. Prog. Inorg. Chem. 18, 383 (1973).

48. W. DeW. Horrocks and D. R. Sudnick. Acc. Chem. Res. 14, 384 (1981).

49. D. S. Swieter, private communication.

50. E. C. Baker, G. W. Halstead, and K. N. Raymond. Struct. Bond. 25, 23 (1976).

51. T. J. Marks. J. Organomet. Chem. 203, 415 (1980).

52. A. F. Wells. "Structural Inorganic Chemistry," 4th Ed., Clarendon, Oxford, 1975.

53. L. L. Merritt and E. D. Schroeder. Acta Cryst. 9, 801 (1956).

54. G. A. Barclay, B. F. Hopkins, and C. H. L. Kennard. J. Chem. Soc. 5691 (1963).

55. W. D. Harrison, D. M. Kennedy, M. Power, R. Sheahan, and B. J. Hathaway. J. Chem. Soc. Dalton 1556 (1981).

56. O. P. Anderson. J. Chem. Soc. Dalton 2597 (1972).

57. F. S. Stephens. J. Chem. Soc. (A) 2081 (1969).

58. R. Restivo and G. J. Palenik. J. Chem. Soc. Dalton 341 (1972).

59. M. Elder andD. Hall. Inorg. Chem. 8, 1268 (1969).

60. E. M. Chadwick and D. Hall. J. Organomet. Chem. 25, 91 (1970).

61. A. R. Al-Karaghouli and J. S. Wood. Inorg. Chem. 10 2293 (1972).

62. A. Griffiths. J. Cryst. Mol. Struct. 1, 175 (1971).

63. M. G. B. Drew and J. D. Williams. J. Chem. Soc. Dalton 1830 (1973).

64. P. G. Harrison, T. J. King, and J. A. Richards. J. Chem. Soc. Dalton 1723 (1974).

65. W. Clegg and P. J. Wheatley. J. Chem. Soc. Dalton 511 (1974).

66. W. Clegg. Acta Cryst. B32, 2712 (1976).

67. D. C. Garner, B. Hughes, and T. J. King. J. Chem. Soc. Dalton 562 (1975).

68. B. N. Figgis, B. W. Skelton, and A. H. White. Aust. J. Chem. 31, 57 (1978).

69. W. Fitzgerald and B. J. Hathaway. J. Chem. Soc. Dalton 567 (1981).

70. K. Yanagi, Y. Ohashi, Y. Sasada, and H. Kobayashi. Bull. Chem. Soc. Japan 54, 118 (1981).

71. C. K. Johnson. ORTEP, Report ORNL-3794 Revised, Oak Ridge National Laboratory, Oak Ridge, Tenn. (1965).

72. B. Eriksson and L. O. Larsson. J. Chem. Soc. Chem. Comm. 616 (1978).

73. M. Ciampolini, P. Dapporto, and N. Nardi. J. Chem. Soc. Dalton 974 (1974).

74. G. J. Palenik and D. W. Wester. Inorg. Chem. 17, 864 (1978).

75. D. W. Wester and G. J. Palenik. Inorg. Chem. 15, 755 (1976).

76. D. G. Karraker. J. Chem. Ed. 47, 424 (1970).

77. R. J. Foster and D. G. Hendricker. Inorg. Chim. Acta 6, 371 (1972).

78. L. A. Aslanov, L. I. Soliva, M. A. Povai-Koshits. Zh. Strukt. Khim. 13, 1101 (1972).

79. K. K. Bhandary and H. Manohar. Acta Cryst. B29, 1093 (1973).

80. K. K. Bhandary, H. Manahar, and K. Venkatesan. J. Chem. Soc. Dalton 2318 (1975).

81. D. Grdenic. Quart. Rev. Chem. Soc. 19, 303 (1965).

82. A. J. Canty, N. Chaichit, B. M. Gatehouse, and A. Marker. Acta Cryst. B34, 3229 (1978).

83. A. R. Al-Karaghouli, R. O. Day, and J. S. Wood. Inorg. Chem. 17, 3702 (1978).

84. D. Grdenic. Struct. Stud. Mol. Biol. Int. 207 (1981).

85. D. L. Kepert, D. Taylor, and A. H. White. J. Chem. Soc. Dalton 670 (1973).

86. M. Sandstrom and I. Persson. Acta Chem. Scand. A32, 95 (1978).

87. G. Johanson and M. Sandstrom. Acta Chem. Scand. A32, 109 (1978).

88. G. B. Deacon, C. L. Raston, D. Tunaly, and A. H. White. Aust. J. Chem. 32, 2195 (1979).

89. A. L. Beauchamp, B. Seperas, and R. R. West. Can. J. Chem. 52, 2923 (1974).

90. C. Stalhandske. Acta Cryst. B37, 2055 (1981).

91. E. Dubler, L. Beck, L. Linowsky, and G. B. Jameson. Acta Cryst. B37, 2214 (1981).

92. G. Grdenic, B. Kamener, and A. Hergold-Brundic. Cryst. Struct. Comm. 7, 165 (1978).

93. A. J. Canty, G. Hayhurst, N. Chaichit, and B. M. Gatehouse. J. Chem. Soc. Chem. Comm. 316 (1980).

94. R. T. C. Brownlee, A. J. Canty, and M. F. McKay. Aust. J. Chem. 31, 1933 (1978).

95. B. Kamerar, A. Hergold-Brundic, and M. Śikivica. Cryst. Struct. Comm. 5, 149 (1976).

96. A. J. Canty, N. Chaichit, and B. M. Gatehouse. Acta Cryst B36, 786 (1980).

97. A. J. Canty and B. M. Gatehouse. J. Chem. Soc. Dalton 2018 (1976).

98. A. J. Canty, C. V. Lee, N. Chaichit, and B. M. Gatehouse. Acta Cryst. B38, 743 (1982).

99. J. D. Dunitz and L. E. Orgel. Adv. Inorg. and Radio Chem. 2, 1 (1960).

100. C. C. Addison, C. D. Garner, N. Logan, and S. C. Wallwork. Quart. Rev. Chem. Soc. 25, 289 (1971).

101. M. Ul-Haque, C. N. Caughlin, F. A. Hart, and R. Van Nice. Inorg. Chem. 10, 115 (1971).

102. G. D. Smith, C. N. Caughlin, M. Ul-Haque, and F. A. Hart. Inorg. Chem. 12, 2654 (1973).

103. A. R. Al-Karaghouli and J. S. Wood. J. Chem. Soc. Dalton 2318 (1973).

104. K. K. Bhandary, H. Manohar, and K. Venkatesan. Acta Cryst. B32, 861 (1976).

105. M. E. Harman, F. A. Hart, M. B. Hurthouse, B. P. Moss, and P. R. Raithby. J. Chem. Soc. Chem. Comm. 396 (1976).

106. C. Chieh, G. E. Toogood, T. D. Boyle, and C. M. Burgess. Acta Cryst. B32, 1008 (1976).

107. F. A. Hart, M. B. Hursthouse, K. M. A. Malik, and S. Moorhouse. J. Chem. Soc. Chem. Comm. 549 (1978).

108. M. Bukowska-Strzyzewska and A. Tosik. Inorg. Chim. Acta 30, 189 (1978).

109. J. D. J. Backer-Dirks, J. E. Cooke, A. M. R. Galas, J. S. Elotra, C. J. Gray, F. A. Hart, and M. B. Hurthouse. J. Chem. Soc. Dalton Trans. 2191 (1980).

110. J.-C. Bunzli, B. Klein, and D. Wessner. Inorg. Chem. Acta 44, L147 (1980).

111. J. D. J. Backer-Dirks, C. J. Gray, F. A. Hart, M. B. Hursthouse, and B. C. Schoop. J. Chem. Soc. Chem. Comm. 774 (1979).

112. J. H. Burns. Inorg. Chem. 18, 3044 (1979).

113. A. J. Canty, M. Fyfe, and B. M. Gatehouse. Inorg. Chem. 17, 1469 (1978).

114. A. J. Canty, N. Chaichit, and B. M. Gatehouse. Acta Cryst. B35, 593 (1979).

115. L. Prigant, M. J. Olivier, R. Rivest, and A. L. Beauchamp. J. Am. Chem. Soc. 101, 2765 (1979).

116. J. Hubert and A. L. Beauchamp. Acta Cryst. B36, 2613 (1980).

117. A. J. Canty, R. S. Tobias, N. Chaichit, and B. M. Gatehouse. J. Chem. Soc. Dalton 169 (1980).

118. M. J. Olivier and A. L. Beauchamp. Inorg. Chem. 19, 1064 (1980).

119. F. A. Cotton and G. Wilkinson. "Advanced Inorganic Chemistry," 4th Ed., John Wiley and Sons, New York, 1980.

120. R. B. King. J. Am. Chem. Soc. 92, 6440 (1970).

121. J. L. Hoard and J. V. Silverton. Inorg. Chem. 2, 235 (1963).

122. R. B. King. J. Am. Chem. Soc. 92, 6455 (1970).

123. J.-C. G. Bunzli, B. Klein, G. Chapmis, and K. J. Schenk. Inorg. Chem. 21, 808 (1982).

124. M. A. Porai-Koshits and L. A. Aslanov. Zh. Strukt. Khim. 13, 266 (1972).

125. W. A. Dollase. Acta Cryst. A30, 513 (1974).

126. C. C. Fuller, D. K. Molzahn, and R. A. Jacobsen. Inorg. Chem. 17, 2138 (1978).

127. H. B. Kerfoot, G. R. Choppin, and T. J. Kistenmacher. Inorg. Chem. 18, 787 (1979).

128. E. F. Hasty, T. J. Colburn, and D. N. Hendrickson. Inorg. Chem. 12, 2414 (1973).

129. E. F. Hasty, L. J. Wilson, and D. N. Hendrickson. Inorg. Chem. 17, 1834 (1978).

130. P. H. Merrill and L. J. Maker. Inorg. Chim. Acta. 28, 47 (1978).

131. R. Louis, Y. Agnus, and R. Weiss. J. Am. Chem. Soc. 100, 3604 (1978).

132. R. Robson. Inorg. Chim. Acta 57, 71 (1982).

133. R. Murray and D. C. Smith. Cord. Chem. Rev. 3, 429 (1969).

134. R. C. Barns and R. W. F. Hardy. "Nitrogen Fixation in Bacteria and Higher Plants," Springer-Verlag, New York, 1975.

135. U. Casellato, P. A. Vigato, and M. Vidali. Coord. Chem. Rev. 23, 31 (1977).

136. U. Casellato, P. A. Vigato, D. E. Fenton, and M. Vidali. Chem. Soc. Rev. 8, 199 (1979).

137. D. A. Sullivan. Dissertation, University of Florida (1975).

138. C. Huiszoon, B. W. van de Waal, A. B. van Edmond, and S. Harkema. Acta Cryst. B28, 3415 (1972).

BIOGRAPHICAL SKETCH

Vincent Michael Lynch was born in Brooklyn, New York, on March 21, 1952. He graduated from Bishop Loughlin High School in June 1970. He entered Millsaps College in Jackson, Mississippi, in September 1970. It was here that he first breathed air that he could not see and saw a cow outside the confines of a zoo. He graduated with a B.S. in chemistry from Millsaps in May 1974. He taught P.E. and Junior High School Science at the St. Andrew's Episcopal School in Jackson from September 1974 until June 1976. He entered this university in September 1976. He is happily married and has no children.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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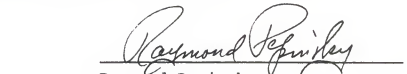

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate Council, and was accepted as a partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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